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REFINER
AND NATURAL GASOLINE MANUFACTURER

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The Look Box

THE crude oil produced from the discovery well in the new field of Sherman township, Isabella County, Michigan has been analysed by the United States Bureau of Mines and found to be a paraffin base oil. The lighter fractions include 40 percent of "gasoline and naphtha" and 20 percent of kerosene distillate. The laboratory analysis indicates that these fractions are more paraffinic than the corresponding fractions from the oil produced in other Michigan fields with the possible exception of the oil from the Trenton lime horizon in Monroe County. The lighter fractions of this oil are more paraffinic than the corresponding fractions from the crudes produced from the Cabin Creek, West Virginia, and the Rodessa, Louisiana fields. The remaining distillates consisting of 23 percent of gas oil and heavier distillates give indications that this Michigan oil would yield about the same type of commercial products as may be obtained from the Rodessa crude oil.

New Crude

The light gasoline, 13.2 percent recovered is of 80.6 A.P.I. gravity. The total gasoline and naphtha, 40.0 percent, is of 65.3 A.P.I. gravity. A 20 percent fraction of kerosene distillates has a gravity of 47.8 A.P.I. and a 10 percent fraction of gas oil has a gravity of 39.0 A.P.I. The distillation yielded 8.8 percent non-viscous lubricating distillation with 36.8-32.8 A. P. I. gravity and 4.7 percent medium lubricating oil distillate with gravity of 32.8 to 31.0 A.P.I. The 14.3 percent residuum has an A.P.I. gravity of 25.4 degrees. The crude oil has a gravity of 48.1 A.P.I. has 0.40 percent sulfur, a pour point below 5° F. and an N.P.A. color Number 5. Carbon residue of the crude is 0.3 percent and of the residuum 2.2 percent.

THE stability of the petroleum refining industry is directly influenced by the crude oil reserve situation. So long as present reserves are maintained, it is believed that stability is assured, but should reserves of crude oil drop materially over a period of a few years, that, then, becomes a different story.

Crude Reserves

It is good to be informed that the United States crude reserves as of January 1, 1937, are estimated to be 12,980,000,000 barrels, as compared to 12,992,000,000 barrels a year ago. These estimates cover the underground supply of crude oil in known United States fields that is extractable by current producing methods. The decline of only 12,000,000 barrels in reserves is so slight that it is of no import. However, due to a large increase in 1935, the known recoverable but unproduced supply of crude is still far in excess of the total two years ago, when reserves were estimated by the American Petroleum Institute as being 12,177,000 barrels on January 1, 1935.

These estimates indicate what the petroleum industry must achieve annually during the next few years. Will it be able to keep pace with the rapidly increasing consumption? To do so, ap-

parently, it must find (unless another East Texas is discovered) around 175 fields per year in addition to new sands and extensions.

It is predicted that consumption of petroleum products during 1937 will exceed that of 1936, perhaps as much as seven percent. Therefore, if the United States petroleum industry is to maintain its oil reserve status it is necessary that more than a billion barrels be discovered annually.

Road Base

TIME and again in these columns attention has been called to the feasibility and the advisability of the proper preparation of road beds or bases through the use of asphaltic road oils. The reasons for advising the advocacy of such practice are two fold. First, by water proofing the road base properly, a longer life is assured the road, and second, the more such waterproofing is done the better becomes the market for such oils. Water is said to be the cause of 90 percent of road bed failures. If the road bed is water proof, state, taxpayer and refinery profit.

Experimenting is underway in various states. Word comes that Oklahoma is working with the process of base stabilization in which asphaltic oil is placed several inches under the surface and allowed to penetrate to the surface. The process is reported to leave a stable and waterproof base on which a bituminous surface can be placed for $1,500 or less per mile.

However, if the total cost for proper waterproofing of base and subgrade of such roads should be around $1,500 per mile, and permanent bituminous topping another $1,500 per mile, the total indicated $3,000 per mile is still remarkably cheap. In as much as the market for asphaltic oils and bituminous products can be greatly increased by successful promotion and advocation of such a practice, it is indicated that refiners producing such road materials should get behind this work and cooperate to the fullest extent. And the public gets better longer-lasting roads at a better price.

Operations

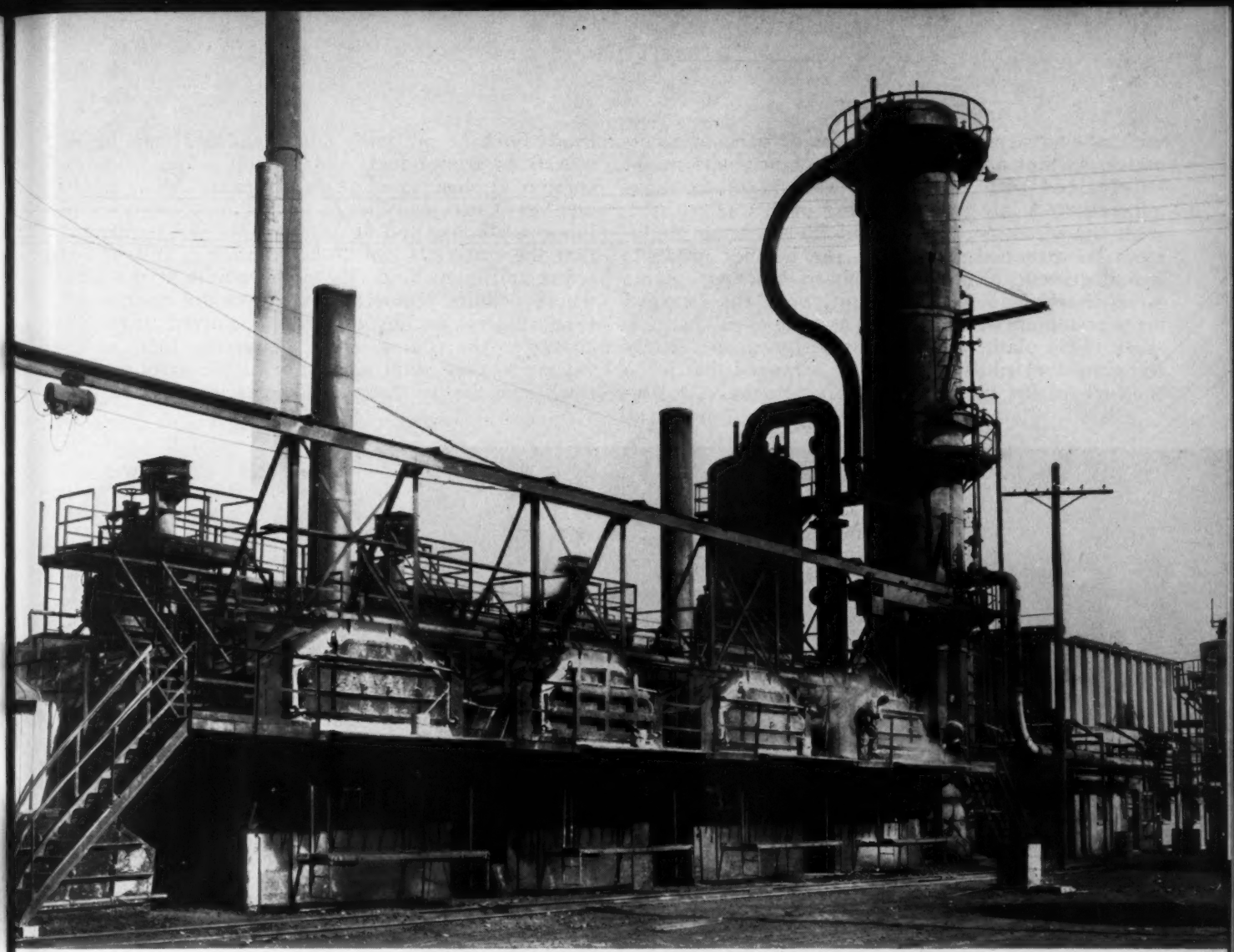
THE refineries of the United States appear to have processed close to 1,100,000,000 barrels of oil in 1936, according to preliminary estimates. This is at an average of slightly more than 3,000,000 barrels of crude charged to still daily. Generally favorable conditions, further improvement of earnings, and various new all time records are in prospect for the petroleum industry in 1937 according to many of its leaders, economists, and students. Although the demand for petroleum was at an unprecedented level in 1936 it appears likely to show a further increase of 7 to 10 percent in 1937. Consequently, petroleum refining should reach new levels, as it did in 1936. If the industry meets with a demand requiring a 10 percent increase in crude oil charges to stills, then 1937 should be a one billion, two hundred million barrel year.

Such prospects contribute much to the present wide-spread activity in construction of refinery equipment of modern type. A recent survey indicates that refinery construction work now under way is in greater proportions than at any similar period during the past decade. Further, refinery construction proposed, under design and actually projected, is of greater proportions than is generally known. One construction company alone recently stated that on its board it had plans for units of a capacity of something like 80,000 barrels of oil a day, installation cost of which will be around $25,000,000.

Purchases

THE petroleum industry is an enormous purchaser. It is the largest buyer of tank cars and of tank ships. It creates one of the greatest industrial markets for steel and iron, motor vehicles, electric power, internal combustion engines, building material, Diesel motors, meters, pumps, pipe, measuring devices, lumber, tanks, rope, gages, cable, paint, hose, cement, rubber, metal products, brass, tin, chemicals, containers, and other products.

Bayway Refinery at Night



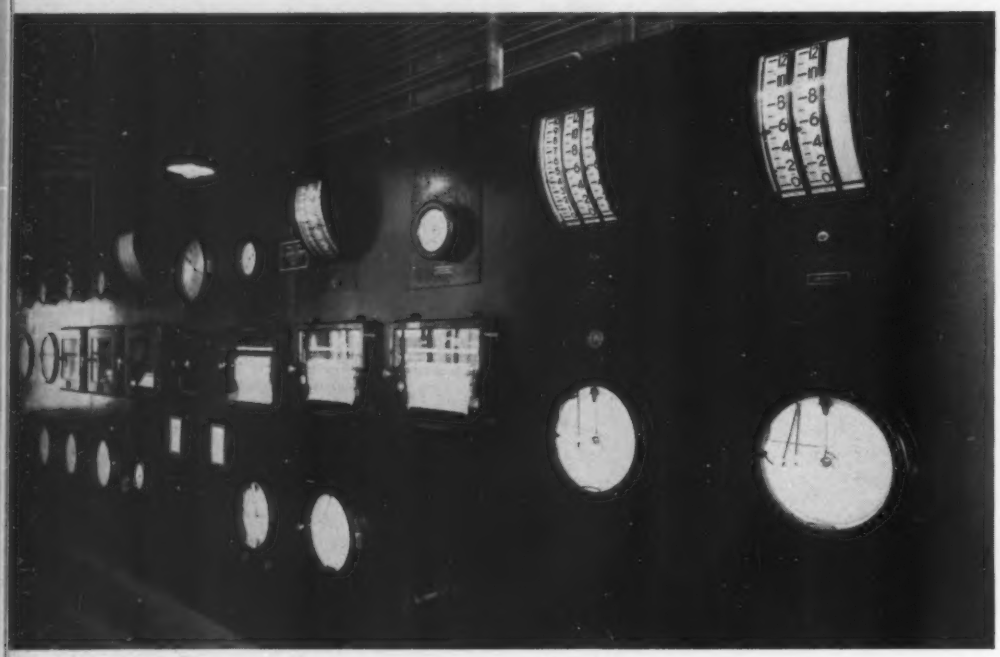
Lubrite's Coke Ovens

and Fuel-Oil Reduction Unit

THE Lubrite Division of Socony-Vacuum Oil Company, Inc., operating a refinery in East St. Louis, Illinois, has been confronted at various times with a slack demand for industrial fuel oil. This fuel is the usual type of bottoms that is manufactured while reducing Mid-Continent crudes by processing them through cracking plants. Being fortunately situated in an area where disposition of a large volume of fuel oil is readily made during periods of industrial activity, and where freight rates are such that good prices may be received, the company can, during these periods of activity, dispose of a large amount of industrial fuel oil. The slack demand for fuel oil usually occurs during the fall months and continues through the winter. However, during these months, the furnace oil market is more active. The refinery runs are not curtailed during these periods, and naturally a reserve of heavy fuel oil is built up which sometimes becomes larger than plant economics warrant.

To overcome this difficulty, it was decided to convert this surplus of fuel oil into a salable grade of coke, and at the same time manufacture other products which might be disposed of advantageously. After a thorough investigation of processes, the decision was made to install four coking ovens together

with a viscosity-breaking unit, with various accessories, so that a maximum yield of products might be obtained with a minimum amount of fixed-gas generation. A late type of coking oven was selected, with the viscosity breaker and fractionating equipment so arranged that when the heavier products manufactured in the vapor-phase cracking plants were charged to the new unit, only the heaviest tarry residuum would be used as coke-oven charging stock. This plant, while being designed specifically to reduce fuel oil to coke, was so arranged that when the fuel market was a deciding factor, the viscosity-breaking unit could be operated independent of the coking ovens, and used as a crude oil distillation plant.



Instrument board in control house.

MODERN INSTALLATION

The type of ovens used when building this plant has been used by various refiners in many sections of the country. However, this installation is one in which all the most modern improvements have been installed, having features not found in many of the older plants of this character. The heating and fractionating units included in the design of the combination plant were designed to process the fuel oil by reducing it to a fraction possessing a very low A. P. I. gravity, and to handle vapors driven from it, as well as the tarry residuum being coked, so that definite products might be removed, having characteristics which would bring a price which would show an operating profit.

The unit as it now stands for operation as a coke plant consists of four ovens, where the heavy tarry residuum is reduced to a solid. There are two principal towers, the first utilized as an evaporator, receiving the oil from the transfer line of the pipe still, or heater. The other is the main column, where the fuel oil fresh from the cracking-still evaporators is pumped in order that a part of the more volatile fractions may be driven from it before it is charged to the pipe still. Also, this column is a fractionating tower so that end point gasoline can be taken overhead. Furnace oil, with minor changes, can be removed as Diesel fuel, and gas oil taken from the column at designated draw-off pans. An adequate number of various types of pumps are located within the pump house and at other points in the plant so that the materials can be kept moving, and furnish reflux and quenching oils to the points in the plant where definite temperatures are to be maintained. Compressors handle the gases evolved from the charge in the coking ovens, delivering them to the vapor recovery plant so that available gasoline fractions can be recovered. The necessary auxiliary equipment for operating the coking ovens, such as electric cranes to raise the doors, coke rams for shoving the finished coke from the ovens, and classifiers for grading the coke as to size, are provided.

OPERATION

When this plant is on stream to reduce the fuel oil to coke and other products, the bottoms from the vapor-phase cracking units, having a gravity of 10 to 12° A. P. I., are charged into the main fractionating column, or bubble tower. They enter this column through the large vapor line connecting it to the evaporator which is equipped with an elbow looking downward towards the base of the tower. Both the vapors from the evaporator and fuel oil from the cracking-unit evaporator being hot, some of the lighter fractions flash off from the charge in the form of heavy vapor. The downward turn of the elbow within the shell of the bubble tower prevents those fractions from escaping upwards into the gas oil draw-off section. Three baffles in the column just above the vapor and charge-line connection control the amount and quality of the fractions removed from the charge. The column is equipped with an inverted conical base so that the heavy oil will readily flow to the outlet connection to which the pipe-still pump-suction line is attached. An electric-motor-driven stirring device is installed near the tip of this inverted cone to prevent what carbon might be in suspension being deposited upon the walls and

eventually clogging the connections. The motor is mounted upon a bracket made of channel iron attached to the side of the column by riveting and located so the shaft of the stirrer can be aligned with the motor shaft, and so the packing gland in the stirring shaft stuffing box can be maintained without shaft weaving.

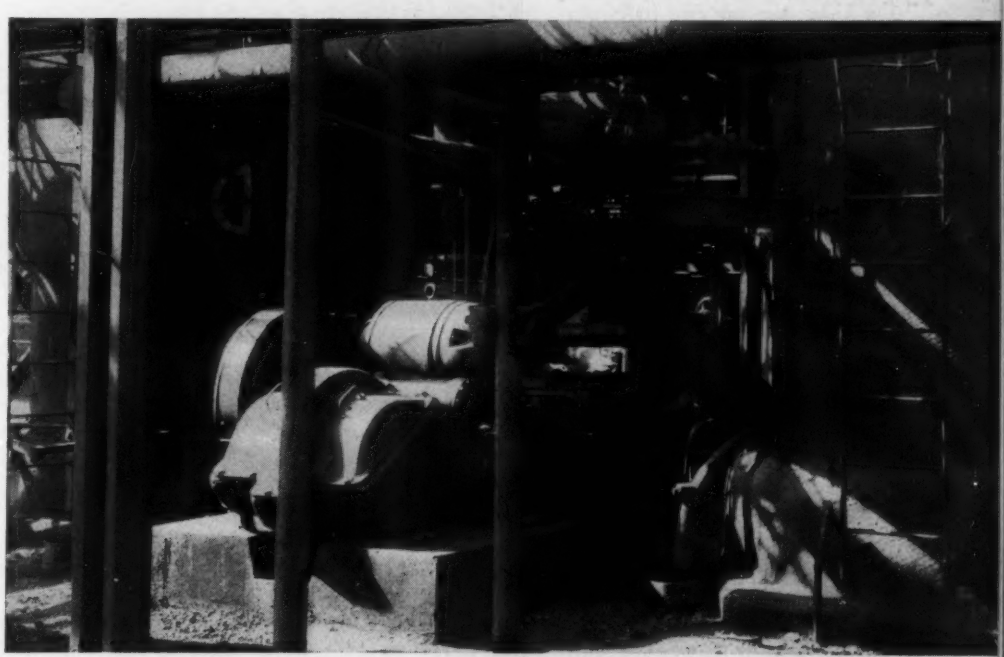
ELECTRIC MOTOR MOUNTING

An electric-motor-driven positive-displacement piston pump takes suction through the bottom outlet of the inverted cone in the bubble tower and directs it immediately to the pipe-still heater. The pump is an outside piston-packed unit, with the motor mounted upon the frame and coupled to the pump with reduction gears. The volume of fluid handled by this pump is controlled by a by-pass between the discharge and the shell of the bubble tower so that a definite rate of flow may be maintained, with excess material being returned to the column. Preheating is unnecessary in the operation of this unit, as the charge handled by this pump has a temperature around 725° F., due to the heat of the fuel-oil charge to the column, and the heat of the coke-oven vapors entering the bubble tower as they leave the evaporator.

The hot oil enters the heater at the lower connection of the convection bank of tubes, passing upward through this section to enter a double row of radiant tubes, to be heated to about 870° F., leaving the heater through the transfer line. The pressure upon the oil in the transfer line is about 100 pounds, gauge, which is reduced as the hot oil flows to the evaporator column. A large portion of this material is immediately flashed into vapors as it enters the evaporator, hot and at sharply reduced pressure. The residuum, having a gravity of from 1° to 2° A. P. I., falls to the base of the column. The vapors pass upward through the column, controlled by three baffle plates near the top, which prevents the passage of the hot tarry residuum from the column. Vapors removed from the charge leave the evaporator at the top where a large vapor line extends from this point to the main column. To prevent distortion of this large vapor line, an expansion joint is installed about midway between the connection at the top of the evaporator and the inlet flange on the side of the fractionator. The evaporator is 9 feet in diameter and 30 feet in height, mounted upon a skirt, which in turn is set upon a concrete foundation. It also has a conical bottom similar to that in the main column, and is equipped with a similar stirring device. Because of the reduction in gravity this tarry residuum has a greater tendency to congeal and stratify than the original fuel oil, and also contains some coke particles formed in the tubes of the heater, which might adhere to the inner surface of the vessel and eventually plug the suction line at the tip of the inverted cone.

OVEN ARRANGEMENT

The four ovens which are used to reduce the heavy, tarry residuum pumped from the base of the tube still evaporator are 10 feet in diameter and 30 feet in length. Each oven is covered with an airtight steel shell to prevent the influx of air and the escape of gases. A common vapor line running across all four ovens, 36 inches in diameter, is connected to a riser attached to each oven near the top center of the arch. The line is laid so it can be connected to the inlet opening of the main column when operating the plant as a coke-production unit, or disconnected when the distillation or fractionating part of the plant is used to reduce crude.

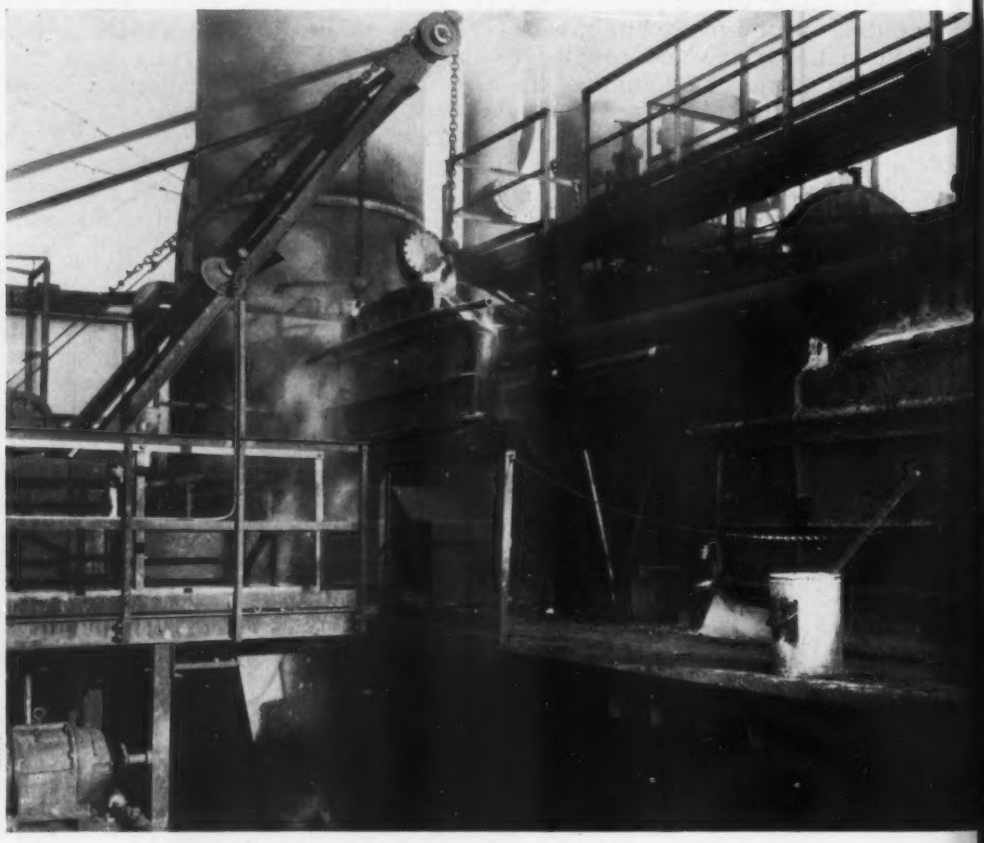


Hot-oil Pump and Agitator.

The arch of each oven is lined with firebrick, while the floors are constructed of carborundum tiles. Channels extend beneath the carborundum floors to act as conduits for the combustion gases. Each oven is equipped with two steel doors, insulated to prevent distortion of the metal and the loss of heat, one at either end. These may be raised or lowered when the operating cycle calls for moving them. Lugs are attached to the top of each door into which hooks may be inserted when using the lifting cranes. A trolley is installed above the discharge end of the oven with which this door may be operated. The

opposite door is operated with a crane which is an integral part of the coke ram car, which is moved along the end of the oven battery upon steel rails. Both the trolley, or overhead crane, and the ram car with its door hoist are operated with electric motors, the wires carrying the current to the first being supported with a steel cable equipped with loops so the wires may be extended across the unit to the farthest oven without becoming tangled or dropping down upon the hot doors of the ovens.

Oven charge pumps remove the heavy, tarry residuum from the base of the evaporator hot and deliver it to each oven in turn as the operating cycle demands. The cycle upon which the ovens are operated is a period of approximately 6 hours, with the 4 units synchronized so that 16 complete charges are made to the coke plant each 24 hours. As there is a short period between the charging of one oven and the cleaning of the succeeding one in which no residuum is being delivered, the oven-charge pumps deliver the tar back to the evaporator through a bypass controller. The pumps are kept moving so the material which they are handling will not congeal in the suction and discharge lines. Sufficient capacity was built into the evaporator so that a considerable length of time is available for any interval between one oven charge and another. The motor-driven stirring device in the base of the evaporator keeps the tar in a state of agitation while it is being recycled so that carbon will not settle out.



The "ram" car equipped with a hoist, the car and its equipment being powered by electricity, lifts the door of the oven to be emptied and pushes the heated mass out

MANUFACTURE OF THE COKE

When one of the coking ovens has been cleaned and made ready to receive its charge of tar, a three-inch nozzle installed in the oven distributes the heavy oil gradually over the carborundum tile floor until a layer has been formed thick enough to seal the joints, which prevents the entrance of combustion gases from the channels beneath. The temperature of the combustion channels beneath the floor at this time is raised to about 2400° F., as the rate of tar distribution is accelerated, so that in about 105 minutes a layer of coke 8 inches in thickness has been formed. The arch temperature at the time of starting the flow of tar upon the floor of the oven is about 1500° F. This temperature is gradually reduced until the end of the coke-forming period has been reached, when the thermometers read 800° F. Furnace temperatures are obtained through the operation of recordr-controller instruments which automatically feed the gas fuel to the burners in the combustion section of the furnace at the rate which will obtain the desired temperatures within the oven and in the coke bed. The drying portion of the coking cycle, in which the coke is formed, continues for approximately 3 hours. During the drying period, and after the coke has been formed, the arch temperature is raised again until it reaches about 1200° F., which, combined with the time factor in the oven, is sufficient to drive practically all of the volatile matter from the coke. Analysis of coke made in this plant shows an average of less than 1.15 percent of volatile matter. The fixed carbon averages about 97.85 percent, with an ash content of 1 percent, and the coke, after it has been removed from the oven, has a dark silvery sheen, dry and brittle.

REMOVAL FROM OVEN

At the close of this part of the operating cycle, the doors which close the oven at both ends are opened by raising them with the electric hoists. The coke side of the oven is operated, when opening the

door, with a boom attached to the ram car, which has two chains connected to cables wound upon a drum. The ram itself operates in a horizontal position upon the floor of the car, being moved with a motor which is controlled from the cab where the operator sits. When both doors have been opened, with the coke car in position with its aprons placed against the runway in front of the oven, the ram is intruded into the oven, and moves, by scraping, the mass of coke from the floor. The car is spotted with the aid of a gasoline locomotive, equipped with a cab to protect the operator from the intense heat of the coke as it falls into the car. This car is equipped with a shield on the side opposite the oven which has dark glass inspection ports so that the movement of the coke can be watched. The coke is immediately quenched by spraying the mass in the car with a stream of water so that the temperature may be lowered below the combustion point. After the coke has been cooled so that it may be safely handled, the coke car is moved to the grader and classifier where the various sizes of pieces are placed in the cars for shipment.

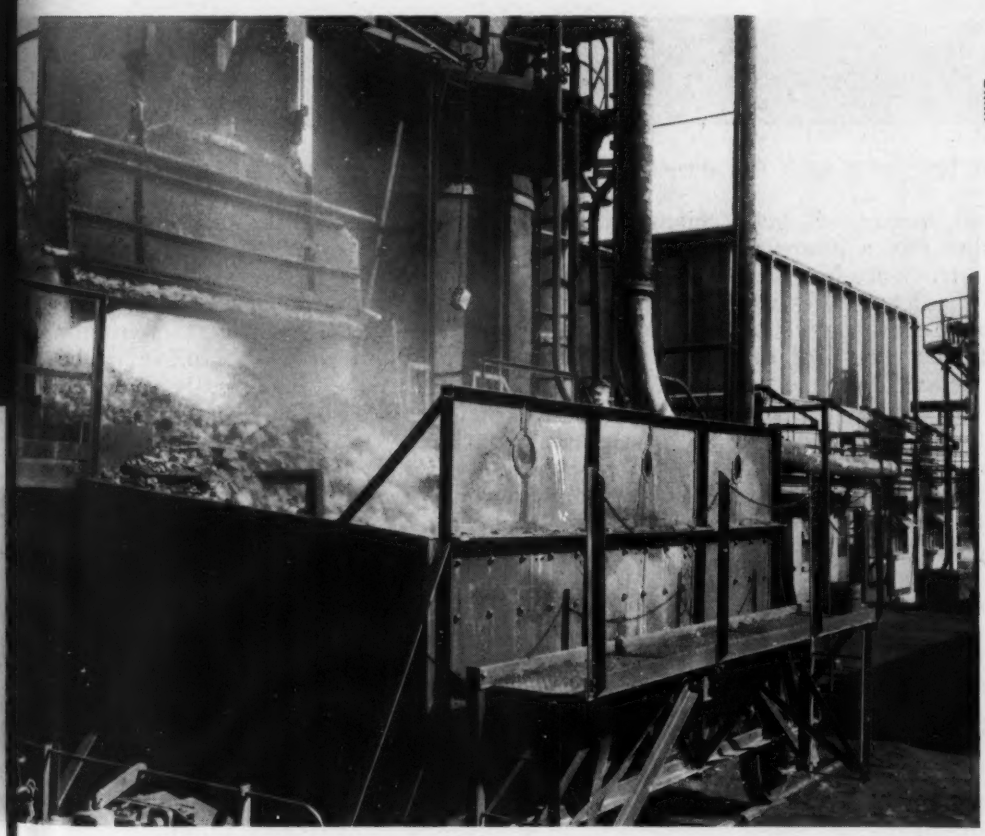
Both doors of the oven are then sealed, after closing, in preparation for another charge of tar. Sealing is accomplished with a mixture of coke breeze and clay, prepared with a consistency of mortar so that it may be applied to the joints around the doors with a trowel. As the doors are being closed, the vapor line opened, and all other lines and controls opened or shut, or connected to the oven, the temperature is raised sufficiently that another charge of tar may be distributed over the carborundum floor. The cycle of operation is continuously repeated so that no appreciable time lag appears between one oven and another. The operating cycle of 6 hours is split up as follows:

Charging time	1.75 hours
Drying time	3.00 hours
Discharging and door sealing	1.25 hours
Total time of cycle	6.00 hours

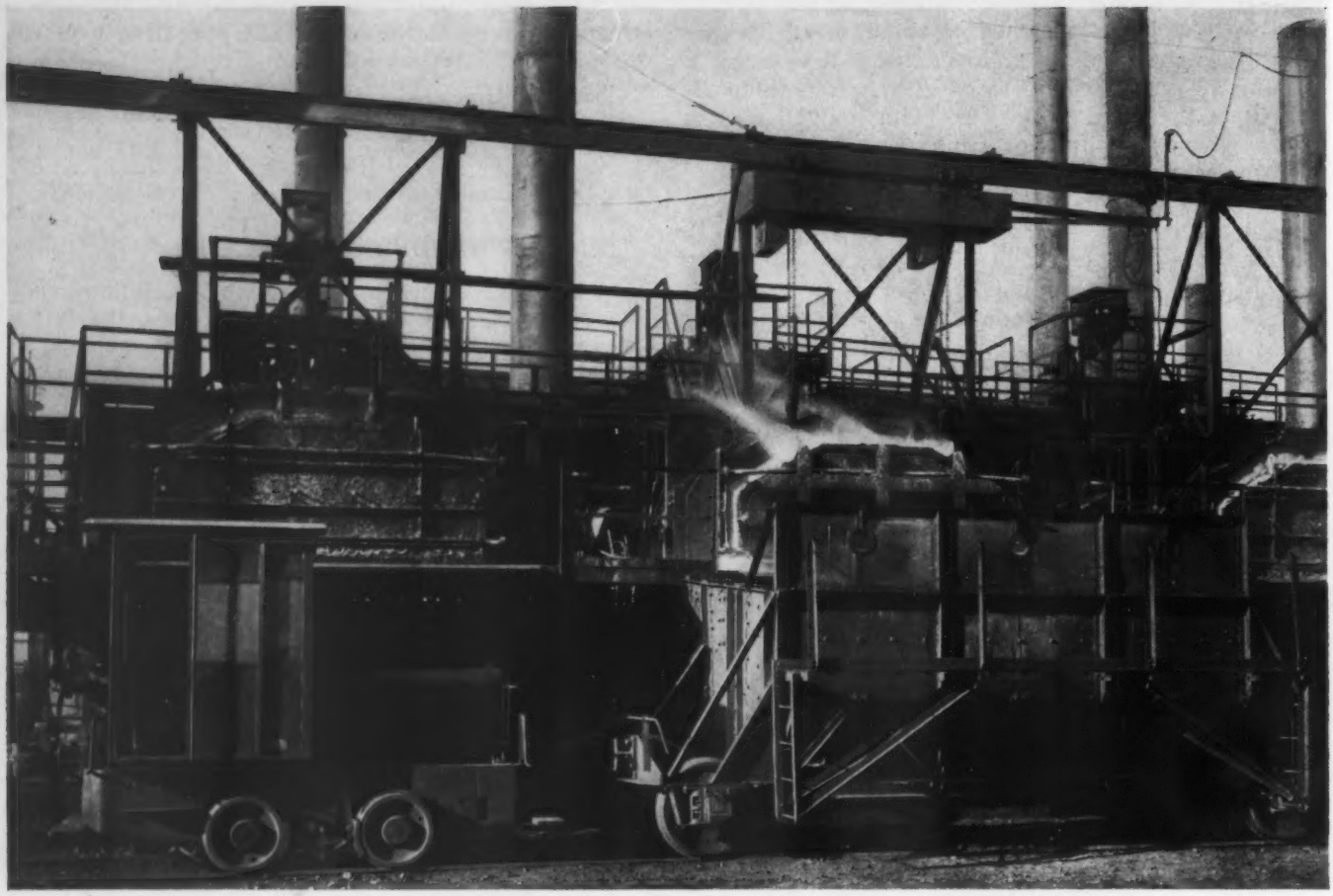
HANDLING OF VAPORS

As the coke ovens provide for the manufacture of two products, coke and volatile fractions, the latter are driven from the oven through the 36-inch vapor line at a pressure approximately zero pounds. In order to obtain accurate control of pressures within the ovens, hydraulically-operated vacuum-control valves are on the vapor risers attached to the arches. The pressure can never, with these instruments in the proper working order, drop below zero pounds pressure, nor rise above a pressure of 1 inch of water. As a large volume of vapor is evolved from the bed of forming coke, naturally some of the very fine solid matter will be carried into the vapor line with the gases. To prevent this material from flowing into the bubble tower, a coke trap is installed in the 36-inch line between the last oven and the inlet of the bubble tower. Gas oil is fed slowly into this line so that a more effectual scrubbing of the gases is obtained than if they were dry. The fluid in the line accelerates the movement of the solid matter so that the line will not become partially choked. Manholes were placed in this vapor line at intervals so that it may be cleaned if any appreciable amount of coke becomes deposited on the inside walls.

The vapors driven from the heavy tar being processed to coke travel directly from the ovens to the main column, or bubble tower, where they are frac-



. . . into a quenching car which operates along a rail track and serves not only as a receptacle for cooling the coke but also as the vehicle for moving it away from the still.



An electric locomotive spots the quenching car at the still door.

tionated into four products: gas oil, furnace oil, gasoline, and dry gas. As this column has a diameter of 9 feet and a height of 65 feet, 12 trays are installed in the upper section so that the gases traveling upward may be fractionated into two separate cuts. A draw-off pan is installed in the tower with 6 of the fractionating trays above and 6 below. Furnace oil is withdrawn from this point in the column, having definite characteristics controlled with liquid reflux pumped back over the column, entering either above or below the draw-off pan. Just below the bubble-plate sections, a closed compartment is built into the column with a chimney extending through the base so that vapors move from the bottom of the column to the fractionating trays above. A closed coil is inserted into the column just above the chimney opening for auxiliary temperature control.

The vapors leaving the top of the column are controlled by open reflux pumped to the column, so the temperature of the vapors average about 235° F. Approximately 7½ percent of the charge is taken from the overhead connection of the bubble tower and condensed as gasoline. Vapors from the drum flow to another vessel which acts as a wash tower so that gases without liquids may be handled by the compressors. The gases from the drums are compressed and treated in the plant recovery unit, where about 3½ percent of the original charge is manufactured into light gasoline which is used for blending.

The furnace oil fraction removed from the draw-off pan between the fractionator plates flows downward to a side stripper, 4 feet in diameter and 14 feet in height, which is equipped with 4 fractionating plates. Steam is admitted into this column in sufficient volume to remove the lighter fractions from the liquid. These vapors re-enter the main column at a point which corresponds to the space between the first and second fractionating plate above the furnace oil draw-off section. With certain minor changes in operation, a cut of Diesel oil may be manufactured, but the furnace oil normally removed has all the essential qualities of a desirable fuel for domestic consumption. The cut represents about 55½ percent of the original charge to the plant, and has the following characteristics:

10 percent	456° F.
90 percent	645° F.
Flash	190° F.
Viscosity at 100° F.	35
Cold test	—0° F.

The cut removed from the chimney section of the column is essentially gas oil, being useful in flushing the vapor line so that coke particles will not hang up at this point. It is also used for diluting the tarry residuum pumped from the base of the evaporator should this product be placed in storage, so the viscosity will be sufficiently reduced that pumping back to the plant may be easily accomplished. During normal operation of the unit, after the gas oil fraction has served its various purposes, it is either permitted to flow from the chimney section, when produced in greater volume than needed, or pumped back to the lower section so that it may be passed through the furnace again with the bottoms from the fractionating column.

The coke produced in the ovens represents about 24 percent of the charge to the plant, and is clean, dry and brittle without staining properties when

handled cold. It commands a premium price on the market, and is readily sold.

When the demand for fuel oil again permits the shipping of this product, the plant is repiped so that the heater and columns may be used as a more-or-less conventional unit for running crude oil. Only a few days are consumed in converting the combination unit from a coking plant to a straight-distillation unit, or back again. Thus, the plant is flexible enough that it will not long remain idle.

Returns from the unit when running the cracking-plant bottoms to coke are said to be sufficient that a price of as much as $1.50 per barrel may be realized, which of course depends upon the selling value of the various products and the cost of the charging stock. When products have been manufactured with definite characteristics, such as the coke, furnace oil and overhead gasoline, the profit realized from the operation depends largely upon the activities of the sales department to secure a constant market for them. The market for this particular grade of coke has been well established, while the market for gasoline, with the characteristics such as are found in the overhead product, depends upon seasonal demand. The large volume of furnace oil might be worked into channels where a demand for it could justify the operation of the combination unit constantly, instead of at times when the fuel oil stocks are piling up.

One feature of the operation of this plant that is instrumental in making for large recoveries is found in the reduction of the usual grade of fuel oil to a very heavy material. When charging ordinary low-gravity fuel oil to coking ovens, the evolution of gases is large, while when charging a product with a gravity of from 1° to 2° A. P. I., gas production is much less. This plant produces only about 11 percent of gas, based on the original charge, when processing the heavy tars to coke. This gas is not wasted, as it is consumed as fuel in the coking ovens, the pipe still and at various other parts of the refinery.

During the summer overhaul of the coking ovens, several changes were made in the method of firing. Each oven is now equipped with double-end fired burners, 9 in each group, each of which discharges into a separate combustion chamber about 10 x 12-inches and 15 feet in length, extending to the center of the oven where they converge to a common flue duct to the stack. It was found to be very difficult to maintain a uniform temperature the entire length of the oven when fired from one end only. Local overheating was found to be centered directly in front of each burner, with diminishing temperatures as gases traveled back through the duct. The temperature differential being found to be as much as 600°F. from the burner outlet to the back of the duct. Each oven was also equipped with a blower and necessary air duct piping to insure a positive and theoretical amount of air for proper combustion of gases. Each combustion chamber was equipped with a flue gas recirculator system designed so the amount of gases to be recirculated could be individually controlled. It is now possible, with proper adjustments, to maintain an even temperature throughout the length of the combustion chamber, allowing a more even and rapid heat transfer to the coke bed above.

Final movement of coke from the plant is on this conveyor.

Boiler Feed-Water Level Control . . .

J. A. CAMPBELL*

THE boiler battery is the heart of the gasoline plant. A steady, dependable supply of dry steam at constant pressure is vital to operating a plant at maximum efficiency. If steam is used as a means of circulating the absorption oil, either a slight drop in pressure or an increase in the moisture content will slow down the circulation rate. Even a slight change in the rate of oil circulation will adversely affect extraction far beyond any accounting through known laws governing absorption.

Many years ago it was the writer's privilege to be engaged in some of the first experimental work done in California in connection with the absorption process. He was operating a miniature absorption plant containing all the units of a modern installation, with the exception of a stabilizer. A very capable mechanic was provided as an assistant. He was supposed to control the fire under the still, hold a steady oil rate, drain the water, gauge the production, hold a steady back-pressure, and keep the gas engine running. And keeping the gas engine running in those days was more of an art than a routine, as it is today. It is obvious that this assistant, in addition to being a mechanic, was a back-pressure regulator, thermostatic controller, and pump governor—all in one.

It was the duty of the writer to record periodically all temperatures, pressures, and rates; and at the end of the run to compute the results. Very soon, however, it was learned that the factor more responsible than any other for erratic results was a varying oil rate. Decided variations in extraction would occur even when circulating at a very high oil-gas ratio. As a result of this discovery, the routine soon developed into the writer taking over all the duties of his assistant so that that worthy gentleman might sit on a nail keg from nine in the morning till three in the afternoon, with one hand on the control valve and the other holding a stop-watch. Each minute would see the same number of gallons of oil, to the second decimal point, pass into the absorber.

One of the largest factors in maintaining steady steam flow is steady boiler feed. The best assurance of dry steam in your main is the carrying of a steady low level in the gauge glass.

Mechanical design in general has undergone vast improvement within the past ten years. Great progress has been made in well drilling, in absorption plant and refinery design, in automatic pressure and temperature control, and in the design of apparatus and equipment having to do with all manner of industrial processes.

ERATIC VARIATIONS IN EXTRACTION

Some months ago the writer became very much concerned over the erratic variation in the extraction curve of a gasoline plant under his supervision. Having checked everything through the absorption plant, it was found there was nothing to indicate the cause, save, possibly, the oil-rate chart. This was not as smooth as it might have been. Since reciprocating pumps were used for oil circulation, the boilers were checked for constant quality of steam and uniformity of pressure. Formerly these boilers had been equipped with automatic feed-water level controllers. However, since the manufacturer had gone out of business and no repair parts could be obtained, the apparatus in time required all the attention common to orphan products. Pampering in this particular case called for regrinding of the valve seats until they were entirely worn out. At length the inevitable happened; the regulators were taken out of service and the boilers were operated once more by hand control.

Self-preservation is the first law of nature, so it is natural for any fireman to carry his water high for safety. High water, nevertheless, means wet steam, and wet steam slows down pumps, cuts lubrication; wears out liners, rings, and pistons; and plays havoc in general with packing. Moisture in steam has no latent heat value and is conducive to leaks and pipe disintegration, and throws an extra burden on separators and traps.

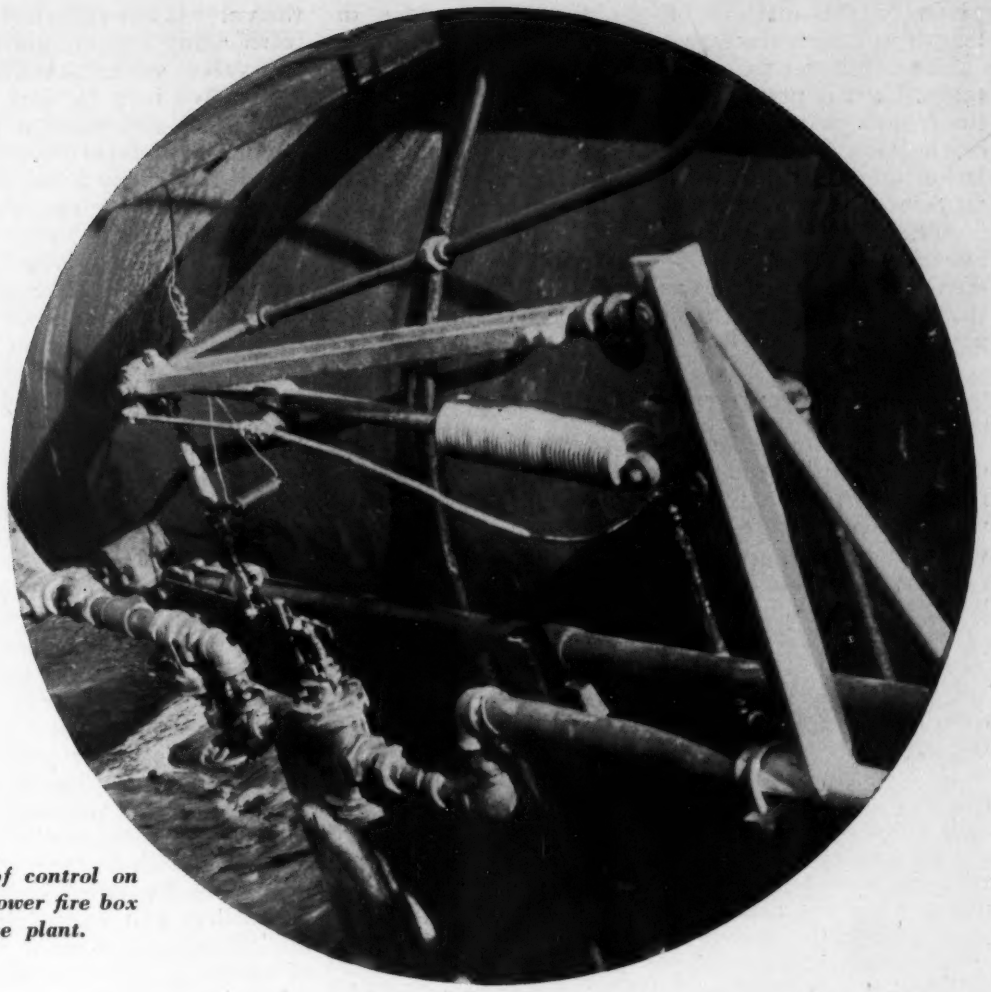
When water rises too high in hand-operated boilers, it is customary for the operator to blow the boiler down—a procedure that not only causes a great waste of water, but a waste also of all the heat built up in that water.

With further reference to the boilers mentioned, they are equipped with high-and-low whistle alarms of the float type. But the upper float is set so high that wet steam results before the whistle will sound. If the level rises very slowly, enough water will prime over to take care of the excess, and a boiler will carry for hours, delivering wet steam, yet with the level just short of the whistle point.

It was decided that what was needed was a new design of regulator, more sensitive and more positive than any then available on the market. Consequently, we set out to design such a regulator.

As the basic principle of the new design we adopted the inclined thermostatic tube, primarily because of the latent power available for the motivation of the feed-water valve. This power is restricted only by the elastic limit of the metal utilized. Since the affectiveness of a thermostatic tube depends on its terminal temperature difference, the initial step was to install a simple tube, equip it with thermometers and determine what this difference was. Such a tube, 42 inches in length, with a slope of 1 to 12,

* Presented before the January, 1937 meeting of the California Natural Gasoline Association, Los Angeles.



Showing installation of control on one of nine 85 horsepower fire box boilers in gasoline plant.

was set up, with the water level cutting its mid point. The boiler was of 150 horsepower, operating at a pressure of 145 pounds, carrying a 3½-inch level in a 12-inch gauge-glass. The average temperatures, taken hourly over a 72-hour period, were 356° F. at top of tube and 268° F. at bottom.

This 88 degree difference seemed surprisingly low and accounted for the poor performance of this type of regulator. Just why was this difference so slight? Let us analyze the situation. Obviously, there are two contributing factors. First, the steam lead coming down from the top of the column is usually uninsulated, and, being a small line, permits condensaation of a considerable amount of steam. The resulting hot water has no path to follow, other than down through the thermostatic tube. As a consequence, the lower end heats up. Second, the steam in the upper end of the tube heats it very hot, and, brass being and excellent conductor, this heat is transmitted to the lower end. The only off-setting factor to nullify this tendency of the lower end of the tube to heat up is the small amount of radiation from the tube's surface.

In an effort to correct this condition, we designed an upper end-casting with a catch-pocket underneath, and ran a copper tube from this drip entirely around the thermostatic tube, connecting it with the water return at the lower end. This hot by-pass dropped the temperature of the lower end of the tube 31° F. Encouraged by this marked improvement, and observing that our level now stayed within the range of the middle 16 inches, we decided to drain the upper 12 inches of the tube. This reserve, which is normally filled with steam, condenses a considerable quantity of hot water. By cutting in a drip-pocket 12 inches down and connecting it to the hot by-pass, we gained another 19 degrees. However, the lower end was still running hot, owing to the conductivity from the steam. We attempted to cut off this transfer by inserting an insulating flange about 14 inches from the lower end. The results were disappointing, in that the terminal temperature was lowered only 11 degrees. It was difficult to find any material for the gasket with a low coefficient of heat transfer, yet possessing sufficient mechanical strength to be safe. Abandoning the idea of cutting off this heat, we decided to dissipate it by the application of fins to the lower section.

This idea called for considerable experimentation with different types and diameters of fins and with variation in their spacing. The thickness of the metal has a decided bearing on radiation. One must compromise between thinness and mechanical strength. We finally developed a very thin fin, corrugated to meet strength requirements. Obviously, the heat-dissipating surface was materially increased.

The first experiments in finning brought forth some surprising discoveries. The concluding experiments resulted in a fin so spaced as to lower the terminal temperature another 100° F. We now had a tube two and a half times as sensitive as the simple brass pipe, and the next consideration must be

given to the method of applying its changes in length to feed-water valve motivation.

The cantilever principle offers two decided advantages. First it permits considerable multiplication of the length changes depending on the ratio of spread of the two members to their length and the translation of this multiplied length change into vertical movement. Second, there is the increment in exposed, or flooded, tube length, secured by raising or lowering the tube.

We adopted 42 inches as the tube length, and fixed the slope at 1 to 12. The spread is such as to give a multiplication of 8.

FEED-WATER LINE VALVE

The next movement was to determine by experiment the proper type and style of valve to use in the feed-water line. After trying out various types, it was decided to use a single-seated, beveled-disc lever valve. This valve gives a positive shut-off and, in this respect, is preferable to a balanced valve, because the latter, to shut off perfectly, must be adjusted to a rather narrow range of feed-water temperature. There is ample power in the thermostat to close the valve against the differential pressure, which is small, usually between 20 and 50 pounds. Most of the boiler batteries in the industry, except on drilling wells, use governors on their feed pumps, which are set within this range. We have, however, successfully operated the controllers on drilling wells without governors when the firemen insisted on opening wide the steam throttle valve on the pump, and the pump when the rotary is idling, will build up pressure against the valves of over 400 pounds.

When we had completed the development work and had a regulator with which we were satisfied, we built nine of them and installed them on the plant boilers. Levels were set at 3 inches in the glasses and, with no other changes in the plant or in the field to account for it, the extraction increased one-tenth of a gallon. This meant a production increase of 1200 gallons per day. We have effected savings in water, fuel, and pump maintenance, and the steam output of the boilers is steadier than it has ever been, as is evidenced by the almost perfect circles recorded on all the operating charts.

Very small valves are used. Regulators in which the valve stem is attached directly to the tube can open the valve an amount only as great as the actual expansion in the tube. Since this amounts to only a few thousandths of an inch, relatively large valve must be used in order to secure enough peripheral opening to permit passage of the required amount of water. The high velocity through this narrow slot is conducive to wire drawing and scoring of the valve and seat. When bad water conditions obtain, there is danger of complete stoppage through liming up. With thermal efficiency increased to over 2½ and a mechanical advantage of 8 through utilization of the cantilever principle, the controller has more than twenty times as much movement available for valve operation. Consequently we can employ a much smaller valve and open it to a considerable extent. A ½-inch single-seated valve is ample for feeding a 150-horsepower boiler with a 20-pound differential; that is, with 20 pounds greater pressure on the pump discharge than that shown on the boiler pressure gauge. For two reasons we do not use any size smaller than a 1 inch body. First, small piping to the valve is not sufficiently rigid and is likely to give, introducing lost motion between the thermostat and the valve, which lessens sensitivity. Second, a ½-inch valve in a 1½-inch or 2-inch line looks out of proportion and takes a lot of explaining. However, anyone with experience in hand-firing a boiler knows that it takes only a few notches on the wheel to meet the full steaming requirements when a full-line size valve is used, and veteran firemen often cut in a ¼-inch or 3/8-inch globe throttle as a by-pass around the feed valve for fine adjustment. With a 25-pound differential, a ½-inch single-seated valve, open 1/16-inch, will pass sufficient water to meet the full load on a 150-horsepower boiler, and, with sufficient movement to open it ⅜-inch, an ample factor of safety is provided.

Every boiler set-up presents a different problem in level control. Engineers are learning the value of close control in all branches of industrial activity. Several years ago we ordered back-pressure regulators by merely stating the line size and the pressure we wished to carry. If we got within five pounds of our objective, we thought we were doing very well. Today the sales engineer whom we contact wishes to know what the throughput is in nature and quantity, whether the flow is steady or fluctuating, if it is corrosive, whether or not at times we wish complete shut-off, and other pertinent information. Supplied with this information, the sales engineer will deliver a regulator that will hold steady pressure and record on a chart a perfect circle.

So it is with boiler feed-water level control. If you are satisfied with a 3-inch variation, manufacturers of controllers can say: "Here she is, boys; stick her on." But if you want to hold levels within a quarter of an inch, there are a lot of factors that must be taken into consideration. We should know whether it is a single boiler or a battery. If it is a single boiler, a very small lever valve may be placed in the steam line to the pump and controlled by the themostat. With this set-up no pump governor is needed, since the pump speed at all times is just fast enough to meet the steaming requirements. If the plant consists of more than one boiler, a controller is set on each. A pump governor, while not absolutely necessary, is desirable, because of the saving effected in fuel, wear and tear on liners, pistons, rings, packing, and gaskets. From a safety angle, also, they are highly desirable, since most boiler-feed pumps are capable of delivering against 400 pounds, which is rather high for 200-pound and 125-pound fittings, which are often used. We should know whether the boiler is fire-box, H. R. T., or water-tube, and whether the load is steady or fluctuating. For extremely steady loads we reduce the movement between the thermostat and the valve. For moderately varying loads we connect direct, and for widely fluctuating loads we multiply the action. These variations are attained by attaching the rod from the thermostat to different points on the valve levers.

If the water is especially bad we recommend a valve with stainless steel trim, more expensive, but at times well worth the difference.

SETTING OF REGULATOR

More important than anything else, perhaps, is the proper setting of the regulator. This does not present any problem on H. R. T. or water-tube boilers, since these are always equipped with water columns.

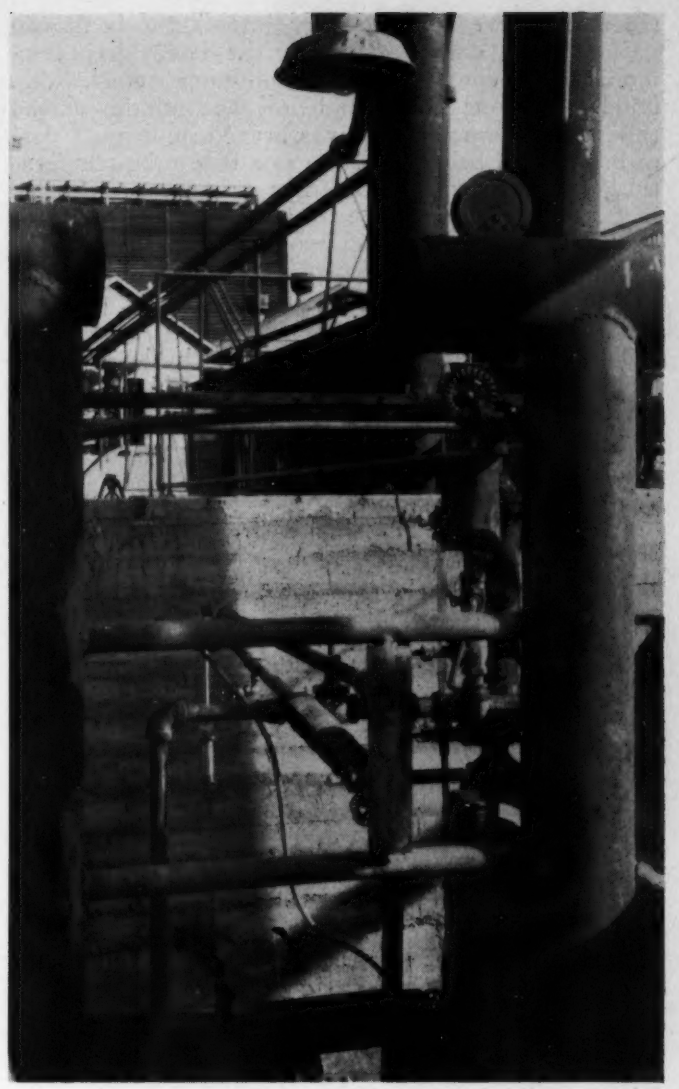
Locomotive type, or fire-box boilers, as they are called in the oil fields, have no columns. The gauge glass fittings tap the boiler shell above the crown-sheet through the head. For some unknown reason, somebody started the practice of tapping in the return line for water regulators down on the side of the water leg. You will find this the case with most of the field boilers that have ever been equipped with regulators. This tap-in is often as much as 20 inches lower than the lower gauge glass fitting. Sometimes this tap-in is in the front, but usually from 10 to 18 inches lower than it should be. The improper location of this tap has been responsible to a large extent for the poor performance of thermostatic controllers on fire-box boilers. Assuming that this water return is tapped in 20 inches below the bottom gauge glass fitting and that the gauge shows the level 3 inches in the glass, if the boiler is steaming heavily, the froth level in the boiler is approximately 1 inch higher. The water in the boiler is full of bubbles of steam and is frothed up about 20 percent higher than the stable balancing column in the gauge glass. Now if we tap in at a point 24 inches below the level in the gauge glass and run a line up outside the boiler and connect it with the steam space, the level in this line would be 5 inches below the level inside the boiler.

There are undoubtedly some of you who have tested gas by means of the Newton tester. Do you not remember how you carefully filled the barrel with so many cc.'s of mineral-seal oil and set the movable gauge with the "zero" at the level in the gauge glass? Then do you recall how, as you turned the gas in, this level took a sudden drop? Surely, there was the same amount of oil in the barrel as before. In fact, there was a little more, for some of the oil in the glass had disappeared and had no place to go, save into the barrel. But the oil in the barrel was frothed up and its weight was partially supported by the buoyant effect of the rising bubbles. Consequently its static head could be balanced by a lower head of unfrothed oil.

This same effect takes place in the boiler. If under the foregoing conditions we set the regulator as we would for an H. R. T., where the water column and the controller each have the same connections when the boiler was steaming heavily, the water would draw down entirely out of the tube, opening wide the feed valve; and it would not shut off until the water was out of sight above the top of the upper fitting. The only remedy for a case like this is to set the regulator 5 inches low. But then the level in the tube, provided the load varies, will run over a wide range, even assuming it remained constant in the boiler gauge. Such a condition makes for poor control, even with a good regulator.

For steady level control, the water return should tap into the boiler at the same level as the lower gauge glass fitting.

In line with usual practice, we have provided a bow-down in this water lead in the form of a T, with a valve to atmosphere. It has been the practice to periodically close the valve in this line next to the boiler and open the blow valve to the atmosphere. This procedure sweeps steam through the entire length of the tube. It does, on starting up a boiler, eliminate all air, which, of course, would insulate the tube from steam condensation and prevent its working. In my personal opinion, the value of blowing the regulator at short intervals is questionable. If the level is properly controlled and the boiler is not priming, comparatively pure water condensed in the steam lead and the upper working reserve runs down the by-pass and returns through the water lead to the boiler. If you blow the system down from a valve located near the point of return to the boiler, you lose all this clean condensed water and replace it by a back-flow of dirty concentrated water from the boiler. I am not convinced that it is not better to blow the tube at intervals of several days.



Typical set-up on 70 horsepower horizontal return tube boiler.

Of course when the steam lead and return are connected to the water column, blowing the latter, which is essential routine, will blow the regulator and the blow-valve is not necessary.

In any case, when the tube is blown with steam, it should be shut off very quickly after the steam comes out; since, if allowed to pass through for any length of time, the steam will heat up and fully expand the tube. In expanding, it opens the valve and raises the level before the tube can cool down again through radiation.

Now let us check into the mathematics involved,

since this reveals some very interesting facts. To gather these data we set up the latest improved model of the controller on a 150-horsepower H. R. T. boiler. Just one half-inch below the middle of the tube a thermometer well was brazed in, a great deal of bronze rod being used to get a true tube temperature, rather than the contents temperature. Three inches below the point was a similar thermometer well, and one at each end of the tube. A 42-inch gauge glass was connected in, running the full length of the tube, with its fittings tapping into the two end-castings.

The first readings were taken with the level at 3½ inches in the boiler gauge glass, which brought the level in the inclined long glass at the exact center, or one half-inch above the upper of the two intermediate thermometers.

The temperatures of the four thermometers, reading down from the upper end-casting, were, 358° F., 297° F., 268° F., and 147° F.

Next, the control valve was adjusted so as to drop the level exactly 3 inches in the inclined glass. Since the slope is 1 in 12, this should drop the level in the boiler one quarter-inch. But it does not, however. When the end-casting rises, the slope is increased. This increase causes the level to run farther down the tube. The reverse occurs on a rising level, which flattens the slope and causes the water to run out farther, and so cool more of the tube than would be exposed by a fixed slope. This is a decided advantage of the cantilever design, and is one of the reasons why it was adopted. Since the intermediate thermometers were spaced just 3 inches apart, dropping the level in the tube 3 inches brings the lower end of the thermometer into the same relative position to the water level as the other occupied at the 3-inch higher level.

Now, we take our new readings, and get, respectively, 358° F., 324° F., 288° F, and 160° F. From these two sets of figures we learn that the arithmetical mean average increase in temperature of the 3 inches uncovered by the water and exposed to steam was only 23.5° F., and the mean rise for the lower 18 inches, which in both cases was filled with water is 16.5° F., and for the top 21 inches, which in both cases was filled with steam, is 13.5° F. The coefficient of expansion of the tube material is .0000105; and multiplying out, we find the actual expansion of the three sections in inches, and in the foregoing order to be .00074025, .00311850, and .00297675. The total of these is .00683550, or a trifle less than .007 of an inch. I believe it is a surprise to most of us to learn that only a little more than ten percent of this expansion occurs in the 3 inches which changed from a water contact to a steam contact. It was a surprise to me to learn that the tube temperature as much as 3 inches below the water level was so high. This is the effect of conductivity. Another interesting observation is that on checking the second set of readings we see that the upper of the intermediate thermometers, even though measuring tube temperature 3 inches above the water level and at a point where you would expect the steam to be up to full saturation temperature, records a temperature of 34° F. lower than the steam temperature in the end-casting, and this latter is not even up to saturation temperature. This is a result of heat dissipation through conductivity.

Getting back to our mathematics, we found total expansion of .0068350 inches. Since this is multiplied by 8, through cantilever action, the end-casting moves up eight times this amount, or .05468 inches. Now, raising the end of the tube .05468 inches will raise the tube at the water level 18/42 of this amount, which will cause the water to run down the tube approximately ¼-inch. So, had we lowered our level in the boiler glass a full ¼-inch, we should have exposed 3¼ inches of tube to the steam and should have increased our total movement by 1/12 up to approximately .06 inch, or a little less than 1/16 inch. As nearly as we can measure this actual amount, it is 1/16-inch for ¼-inch change in boiler level.

Any slight discrepancy here is easily explained by the fact that the true mean temperatures are not arithmetical means, and our slope increment changes the slope ratio, thus introducing a slight correction. For all practical purposes the mathematics is close enough and, to me at least, was very enlightening.

It will be noted that the lower end temperatures in this series are somewhat higher than those in the 72-hour test. These were purposely taken in the middle of the day when it was hot, with no breeze stirring, so as to determine the movement available for valve operation under the most adverse conditions.

After developing a regulator with such potential movement of the valve mechanism, it was logical that we utilize this movement in operating a high-and-low whistle alarm. If you can hold a very constant level in your gauge class, the whistle will blow only when something goes wrong. For instance, if the feed pump should lose suction or stop from mechanical failure, the whistle will blow for low. Should pump packing, or any other foreign matter, become caught between the disc and the seat of the valve so as to prevent its closing, the level will build up and the high whistle will blow. Since these conditions are unusual, the whistle may not blow for months or years at a time; but when it does, it may prevent the necessity of retubing the boiler or replacing a plate.

The simple mechanism devised permits the setting of the valve trips so close that a variation of a half-inch from normal will sound the whistle. Also, they may be set so as to be independent, permitting more variation on one than on the other. The adjustment is simple, and is fixed by setting a jam-nut. Equipped with this device, a boiler will whistle for high water long before the level has gone up sufficiently to produce wet steam. It can be adjusted to whistle for low, with only a slight drop below normal, thus affording the attendant an opportunity to correct the difficulty before he loses sight of his level in the bottom gauge.

ADVANTAGES OF SYSTEM

The advantages of this system are apparent. First, it is fool-proof. Movement of the operating mechanism is inevitable if the water level rises or falls in the tube. By-passing or completely removing the level-control valve still leaves the whistle in operation. All parts are outside and so are accessible at all times. A complete range of adjustment is provided.

When the alarm is installed, steam for the whistle must be taken from a source other than the steam lead to the controller. Even the small flow of steam necessary to blow the whistle will reduce the pres-

sure in the upper end of the tube, and the full boiler pressure below will force the water up the thermostatic tube and chill it off. If whistling for high, the whistle will blow continuously and keep the water valve shut off till the boiler is dry. If whistling for low, the whistle will give one short blast, then the water will rush up the tube, chilling it and shutting off the whistle. This performance allows the water to run back and the tube to heat up, blowing the whistle again, and repeatedly at short intervals.

This source of steam for the whistle should be from a point in the boiler shell or water column, slightly below the connection in the whistle head, so as to drain back any condensate to the boiler. Otherwise, a small slug of hot water may shoot out when the whistle valve is first opened.

When a rotary is in operation, it would be hard to hear even a locomotive whistle from the derrick floor. This condition prompted the signaling by means of lights. Two small Mercoid switches are mounted adjustably on the lower whistle arm. The electric leads from these on each of the boilers in the drilling battery are connected to a three-wire system running to the derrick floor. Here two vapor-proof lights are mounted, a red one for low water, and a blue one for high water. If any one of the boilers develops low water, the red bulb lights. If any one runs high, the blue light goes on. With this system the driller has a complete check on boiler performance. The adjustment on the switches can be made independent of the whistle, either more or less sensitive. With this arrangement, the whistle and the mechanism can be eliminated, since only one arm is necessary for the tilting of the Mercoids. Or electric horns may be used, or any combination of light and horns. The power, a simple 110-volt lighting circuit lead, can be cut in at any point between the derrick and the boilers. Provision is made for checking at any time the performance of both the whistle and the electric signaling.

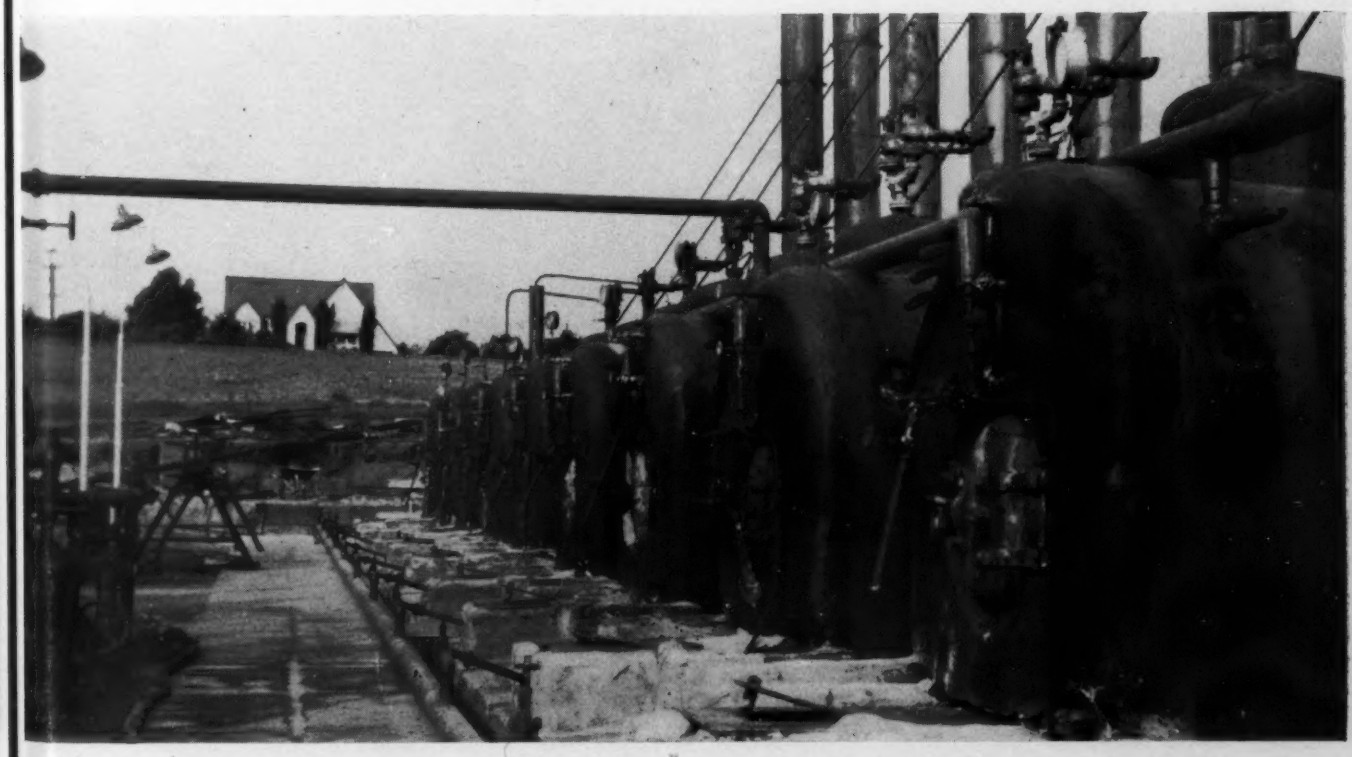
There is one more point I should like to stress with regard to the action of the fins. When the regulator is properly set: as the level drops in the gauge glass, all the water will run out of the tube before the level is down out of sight. This draining fills the entire tube, including the finned section, with steam. The radiation from the fins releases large quantities of latent heat, which heat the tube very hot. This heating causes an extreme opening of the valve, thus making it impossible to burn a boiler, so long as water is available at the proper differential.

There are many applications for the boiler other than in boiler-feed regulation. They are being used successfully for discharging condensed steam from evaporator and stabilizer reboilers. The condensate is discharged at a rate equal to that of formation. and no steam blows through. For such service we recommend stainless-steel-trimmed valves, or, if the service is especially severe, we Stellite both valve disc and seat.

It can be used advantageously for liquid-level control in any location where, above the liquid, there is a hot gaseous component capable of heating the upper end of the working tube. It is especially suited for maintaining a level in stabilizers or reboilers.

Another application we have made, utilizing the cantilever principle but eliminating the fins, is in controlling the gas fire under a small retort in a continuous oil re-conditioning plant. In this installation the entire oil flow from the retort passes through the length of the tube, and the multiplied expansion and contraction effect closely regulates the temperature of the oil entering the small fractionating column.

Battery of nine 85 horsepower boilers in gasoline plant equipped with new controls.



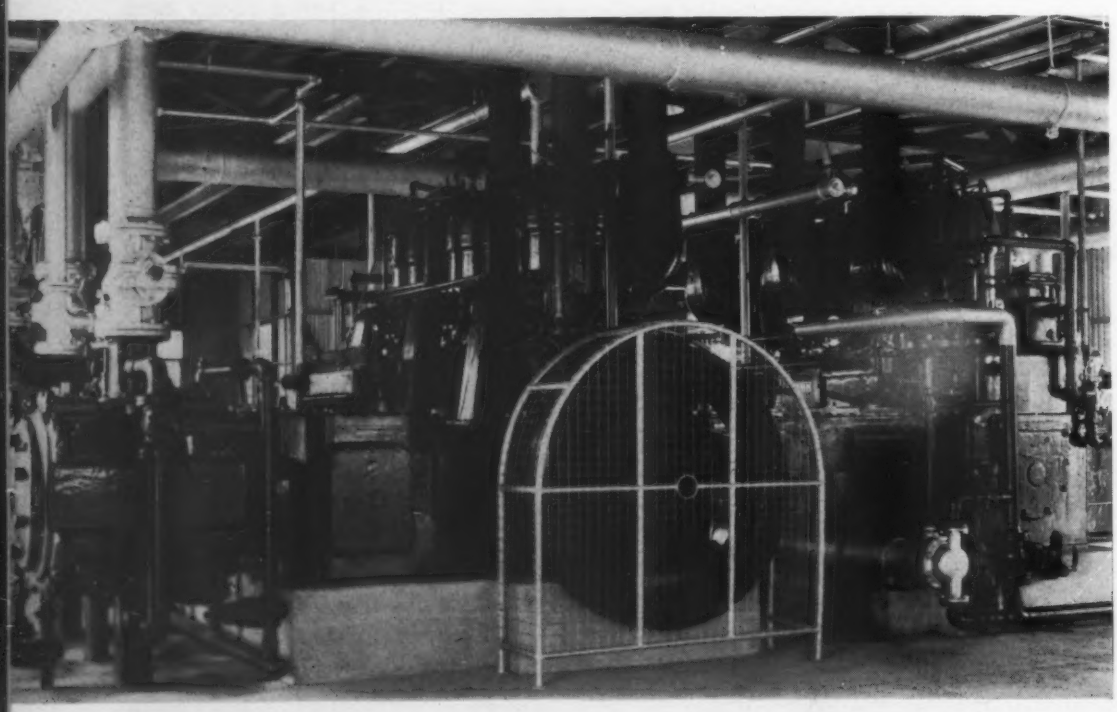
Modern Design *In New Monte Bello* Gasoline Plant

FOLLOWING extension to the old Monte Bello oil field north of Pico, California, Universal Oil Company, with Richfield Oil Company built an absorption gasoline plant to process the gas produced with the oil from partnership wells. A greater part of the plant was made up of new material, especially the compressors and distillation equipment. The engines, vertical three-cylinder, two-cycle units, were among the first of this type to be installed in gasoline plants, being the fifth, sixth and eighth of the series manufactured.

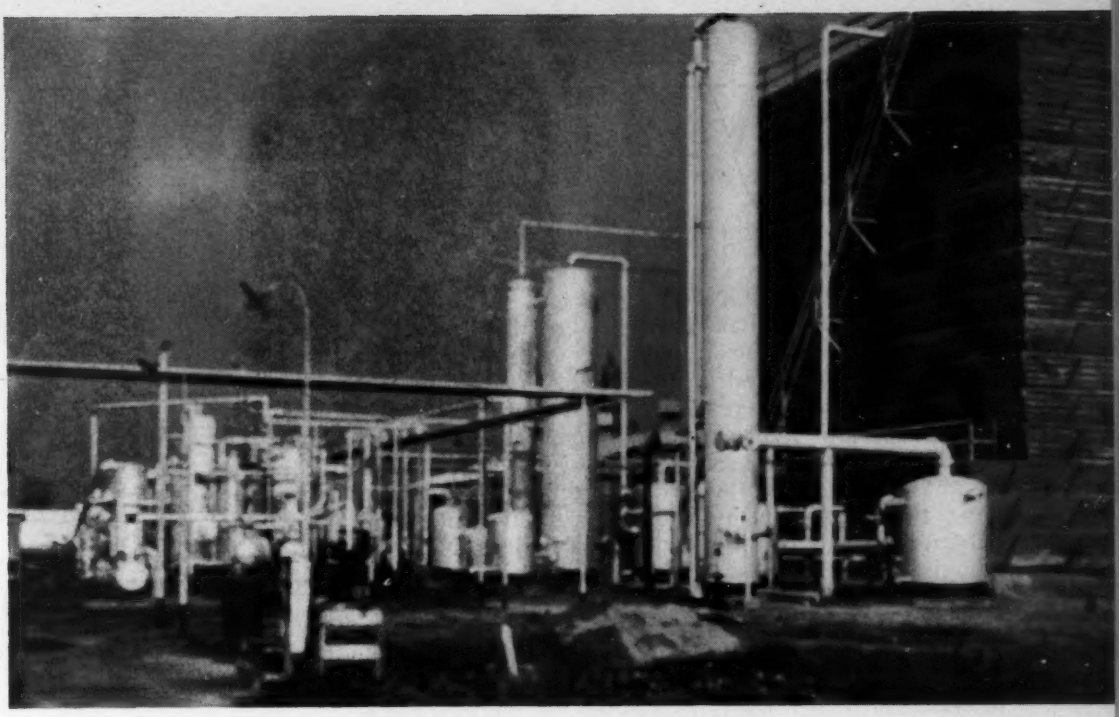
One of the first pronouncements delivered by both companies to the designers and builders was that the plant must be built so the investment would be returned quickly, and should contain no equipment not absolutely necessary to efficient operation. Gas being produced under low pressures dictated that it must be brought in with compressors, and the fuel situation decided that the residue must be compressed sufficiently that it could be introduced into pipe lines for transmission to other parts of Southern California.

Several types of gas engine-driven compressors were considered, keeping in mind that some time in the future they might be moved to other fields and those desired must be compact enough to permit trucking easily and with the least amount of dismantling. The engines selected have power cylinders 13½ x 14 inches, placed vertically above the bed plate, with the compressor cylinders laid horizontally. Each engine is equipped with two cylinders, having a bore and stroke of 17 x 14 inches, respectively, while the third, for medium high pressure work, was smaller in diameter, being 11 inches inside.

Two of these machines were installed in the plant with their backs facing each other, with sufficient space provided in the building for the fourth unit, which may be installed in the same manner and backed up to the third unit. The foundations for each engine rests upon a concrete mat, poured to cover the entire floor, sufficiently strong to support the engines without the need for deep excavations. The character of the soil in this part of California is such that water may be secured by digging shallow wells, which was partly responsible for the type of foundations decided upon. These engines obtain lubrication by forced feed throughout, with the oil circulated through external coolers to maintain low temperatures. Each engine is equipped with an individual oil cooler, which is of the shell-and-tube type, mounted upon the foundation block



Interior of engine room, Universal Oil Company's gasoline plant, Pico, Cal.



Universal Oil Company's gasoline plant in the Monte Bello extension, north of Pico, California.

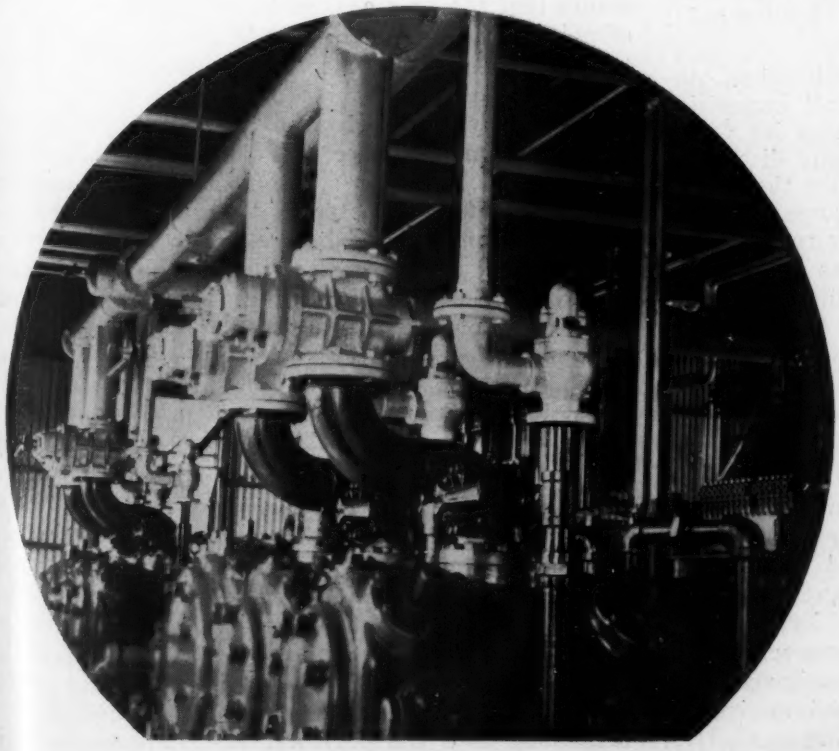
beside the unit. Water is circulated through the coolers to obtain the required temperature on the lubricating oil.

Intake headers were supported above the compressor cylinders, with short nipples between them and the control valves, which are of the ball bearing, venturi type of lubricated plugs. Two welding ells were used, with a reverse curve made by inverting the turns, so that the headers might be connected to the intake ports, and not be directly above them. The lubricated plug valves have flanged bodies so removal is made easily, should repairs or replacement be required. Safety valves are installed on each side of the unit, attached to risers welded to the discharge headers with the vent line leading through the roof of the building to disperse the gas to the atmosphere when the valves function.

Due to the fact that the soil in this vicinity is somewhat sandy, and the wind currents vary during the day, a certain volume of abrasive material is carried by the air, which when taken into the compression chambers of the power cylinders, might cause excessive wear. To intercept this material, air filters were installed on each line, which were installed at the eave height of the building. These cleaners are of the oil type, utilizing a combination of centrifugal force and washing.

The absorption and distillation equipment consists of units employing the usual type of flow, with the absorber 4 feet in diameter, by 40 feet in height. Circulation is obtained by using steam-driven reciprocating pumps, which handle rich and lean oil and cooling water. The conventional type louvre tower is one of the few pieces of equipment that is not new, but when dismantled at the point of previous operation, it was found to be sound and in good mechanical condition.

After passing the gas through the absorber to remove the desired hydrocarbons, approximately 1.00 gallon per thousand cubic feet, the residue is taken into the small bore, high-pressure cylinders of the engines and pumped into the transmission line of one of the gas companies operating in that district. Approximately 125 pounds are required to dispose of the surplus fuel.



Intake header arrangement.

Polymerization . . .

An Important Factor In Refining Processes

R. FUSSTEIG
Jaroslaw, Poland

POLYMERIZATION, an important factor in refining processes, has been known from the beginning of the oil refining industry. The first distillation processes encountered a great deal of difficulties which were but the results of polymerization reactions of certain hydrocarbons. During long heating of the crude in shell-stills certain higher molecular weight hydrocarbons were subjected to decomposition; these split-up hydrocarbons then underwent polymerization, forming larger molecules. Oil technologists have been searching for methods to avoid these difficulties. Studies encouraged the development of more efficient distilling methods, and the continuous shell-still battery came into use, and with it came dephlegmators, partial condensers, baffle towers, and other inefficient types of rectifying apparatus. With the adoption of the bubble-deck and the controlled reflux tower, rectification reached a high degree of efficiency. The shell-still with its rectifying column was supplanted by the tube-still, and the modern fractionating column, which provides not only rectification, but stripping as well. But even with the most efficient distilling apparatus, it was found that the characteristics of the product were governed by the nature of the crude from which the product was produced. It is true that the easily polymerizable higher molecular weight hydrocarbons are not so easily split up, under the new distilling conditions, but they are subjected to other reactions during long standing; these reactions induce the formation of compounds of asphaltic and resin-like nature. In other words, these hydrocarbons cannot be separated from the other hydrocarbons by means of distillation, due to their similar boiling-point ranges.

For this reason technologists have undertaken considerations for chemical removal of all impurities from the oil, which ordinarily decreases its value. Sulphuric acid will be the first reagent discussed, and it has been most widely used since the beginning of the refining industry. The treatment of oils with sulphuric acid was introduced for refining animal and vegetable oils, and in 1792 was adopted for refining "coal oils" by Tower in England[1]. Since the beginning of the refining of oils, about 70 years ago, this acid has been applied to the purification of various petroleum products.

However, the chemical treatment with sulphuric acid leads to polymerization of certain hydrocarbons. The unsaturated hydrocarbons with double or more linkages tend to saturate their free linkages. When adding the above-mentioned acid to unsaturated hydrocarbons an acid ester is formed in the first phase; this additional product subsequently reacts with another molecule of the olefin to form a polymer. But there are certain hydrocarbons which are able to polymerize without using sulphuric acid. For instance, the cyclo-pentadiene, C_5H_6, polymerizes at room temperature into di-cyclo-pentadiene, $C_{10}H_{12}$; when increasing the temperature, the above-mentioned di-cyclo-pentadiene further polymerizes to a product which is a hard resin, similar to "sea amber." Styrol, C_8H_8, polymerizes so energetically that considerable heat is liberated.

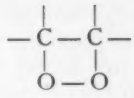
But the majority of unsaturated compounds are not able to polymerize without using a catalyst—such as sulphuric acid. Zaloziecki and Zielinski[2] carried out investigation on Polish crude, free from asphalt, which had a specific gravity of 0.8539/15C., using 5 percent of sulphuric acid. After a period of 80 days, the formation of considerable asphalt had occurred. These investigators proved by the experiments that tars, pitches, coal and coke are products of polymerization. In the coupling of a simple sugar to form the cellulose of cotton or wood fibres, or the conversion of silicic acid to common quartz sand, aluminum hydrate to bauxite, ruby or the sapphire, and in the manufacture of Bakelite or similar synthetic resins, water is split-off during the coupling reaction. But in the case of the refining of hydrocarbons of unsaturated nature, we have polymerization reduced to its simplest terms—that is, nothing is split-off during the reaction. That, then, is true polymerization.

Polymerization may be defined as the union of two or more molecules of a substance to form a larger molecule, the latter being called a "polymer." A search of the literature on polymerization reveals that there are two plausible theories or explanations of the mechanism of polymerization of unsaturated hydrocarbons. The first theory was proposed when technologists were studying the mechanism of sulphuric acid refining of hydrocarbon oils of unsaturated nature, viz., that sulphuric acid first forms an ester, such as alkyl sulphuric acid (acid ester) by addition; this addition product subsequently reacts with another molecule of the unsaturated hydrocarbon to form the polymer. The sulphuric acid is

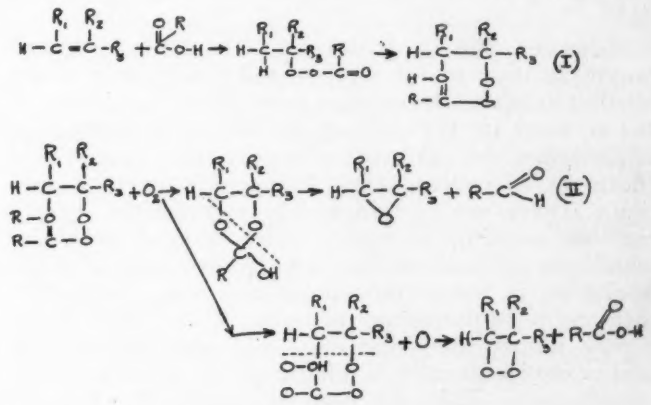
liberated, and theoretically may go through many cycles. The second theory is called the "partial valence" theory. According to this theory, the doubly-linked carbon atoms have partial valences or residues of free affinity. The further assumption is made that the molecules contain a mobile or labile hydrogen atom which shifts from one molecule to the other, thus permitting polymerization. This explanation may account for polymerization in the presence or absence of catalysts where no addition compounds are formed. According to either of the above theories, two unlike molecules may also react—thus explaining the formation of the higher polymers. Under certain conditions the saturated and cyclic compounds are able to combine with concentrated sulphuric acid, being transformed to acid esters. This reaction causes certain quantities of the above-mentioned hydrocarbons to enter into polymerization with other unsaturated hydrocarbons. If we now inspect, for the sake of comparison, the behavior of hydrocarbons during refining with concentrated sulphuric acid, we will find that this process shows a great number of very undesirable features. First of all, it must be stated that during refining in this manner certain sulphonic acids are produced which cannot be eliminated from the oil due to their insolubility in water and their solubility in oil. These sulphonic acids are able during long standing, or during the lubrication of an engine in the case of motor oils, to polymerize and act on other hydrocarbons as catalysts for their polymerization; the reactions produce in consequence the formation of tars, asphalt and coke in the engine. Furthermore, there are certain hydrocarbons which possess a high degree of "oiliness" properties; these compounds are soluble in concentrated sulphuric acid. Refining with this acid leads to large losses and does not produce an ideal lubricating oil. Investigators have therefore been searching to find methods which remove all impurities from an oil without the attendant polymerization reactions in the past. They have displayed an increasing activity in the physical-refining field, which has resulted in the development of several solvent-refining processes. This new method is based on the fact that saturated hydrocarbons are insoluble in the proper type of solvent. In other words, the naphthenic, aromatic, asphaltic hydrocarbons, as well as sulphur and nitrogen compounds, and impurities in general, are soluble in the solvent. Of course, such physical extraction causes no polymerization to take place, and therefore such treated oils have been shown to be well balanced, high grade lubricating oils, capable of resisting oxidation, sludge formation, carbon deposition, and extreme viscosity-temperature variations. Physical refining as an auxiliary step in the manufacture of special oils such as turbine transformer, electric refrigerator, airplane, and white medicinal oils and the like has demonstrated its high degree of effectiveness.

However, there are lower molecular weight hydrocarbons, such as the gasolines, which usually cannot be refined with the aid of the above mentioned solvent procedure, because the boiling ranges of the solvents are quite similar to those of gasolines. Therefore, sulphuric acid has been used almost exclusively in the refining of light oils. Especially the cracked petroleum products must be treated to remove the compounds which are the cause of gum deposition; gums which settle out of the cracked gasoline in storage tanks, in the motor carburetor, clog the fuel system, and form deposits on the hot parts of the engine, on the stems and seats of the inlet valves, in the intake manifold, and so forth, and often result in loss in anti-knock properties of the gasoline. The chemical nature of gum, as well as the mechanism of its formation, has not yet been thoroughly explained. But it is accepted by many investigators that gum is a product of polymerization reactions.

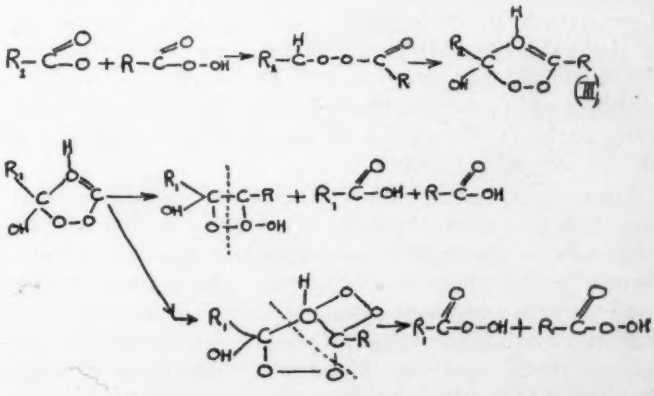
Gum is primarily a product of the auto-oxidation of unsaturated hydrocarbons, such as the mono, di and tri-olefins. The rate of gum formation is known to increase with the concentration of oxygen, rise in temperature, presence of deleterious substances of foreign nature, and with exposure to actinic light. The action of atmospheric oxidation in the olefinic bonds causes the formation of the peroxide:



in the first phase; this then undergoes change into aldehydes, ketones, acids, and so forth. Let us now present a simple scheme of reaction for the mechanism of gum polymerization:



Thus through the medium of reactive oxygen compounds of type I the per-acid would be regenerated along with the hydrocarbon peroxide II, which latter can break into an aldehyde and ketone, the aldehyde being then further oxidized in the presence of per-acid, as follows:



The compounds of type III play a minor role in residual gum formation. They show an intense peroxide reaction, but give comparatively little gum. The compounds of type I when heated in non-

aqueous solution would tend to form glycols, which would then polymerize with the expulsion of water to form gums. It is seen from the above that oxygen plays a very important part as a catalyst in the intermediate reactions of the polymerization of di-olefins. In other words, the ideal or the absolute absence of oxygen or oxygen compounds hinders the reaction of gum formation. It has been stated by the author that when gasoline (cracked) was kept in tightly closed bottles out of contact with air there was no color change or gum formation to any great extent, but that when the same material was exposed to air it darkened rapidly and soon deposited gum. To prove the correctness of this phenomenon, studies using x-rays and ultra-violet light were undertaken. Several bottles filled completely and others partly filled with the gasoline were exposed to the above rays. There was no appreciable effect greater than that found with ordinary sunlight; the reaction rate in all instances was increased, to be sure, but the nature of the change produced seemed to be independent of the light effects. A sample of the gasoline from which the air had been carefully excluded did not appreciably darken, irrespective of light conditions, but a sample that had been exposed to air or other oxidizing agents had darkened and formed gum even when kept in a cool, dark place, though not so rapidly as when the sample was exposed to light.

However, the supposition of the author is that polymerization of the oxygenated compounds is not all that takes place in gum formation. According to the opinion of the author, a direct polymerization of di-olefins also takes place in gum formation. These reactions, of course, take place under proper conditions. There are certain highly complicated hydrocarbons existing in solution in cracked gasolines which act as catalysts in the polymerization of these di-olefins. It seems that these catalysts are hydrocarbons of high carbon content; this carbon is so highly unsaturated that it is not able to combine with a molecule of a di-olefin in any fixed ratio or combination. This reaction is similar to that of sulphuric with the unsaturated hydrocarbons. The above mentioned unknown hydrocarbon reacts in the first place with one molecule of a di-olefin; secondly, this combination reacts with the second molecule of a di-olefin or olefin; finally, a breaking-up between the polymer and the above mentioned higher molecular weight compound takes place. These reactions cause a lowering of the final yield of gasoline, and a degradation in its quality, since a greater amount of the valuable anti-knock olefins are removed from the fuel by this polymerization process. It is the author's opinion that these higher molecular weight hydrocarbons should be removed in the first phase of any refining process.

However, not all types of cracked gasolines contain the above mentioned compounds which act as catalysts in gum polymerization of olefins and di-olefins in the absence of oxygen. The type of crude used plays a very important part. Moreover, the conditions of cracking also influence gum formation by these type of catalysts. The author has observed that the type of gasoline produced in liquid phase cracking is free of these higher molecular weight hydrocarbons, and the above mentioned experiments were carried out with a liquid-phase type of gasoline. Quite another behavior with vapor-phase gasolines has been observed in the absence of air. Here, a change of color is noted even when the gasoline is allowed to stand several days in the absence of oxygen; it has also been observed that gasolines from an oil containing unsaturated hydrocarbons show a greater amount of these unknown hydrocarbons, whereas those from oils of saturated contents contained none or only traces of the compounds. It is therefore seen that unsaturated hydrocarbons may be split up under certain conditions into higher molecular weight compounds soluble in gasoline, these compounds being the catalysts for gum-formation.

Therefore the removal of these compounds must be carried out before submitting them to further processing. For this purpose the clay treating process is used. This process in its present state of development gives good results with cracked gasolines derived from paraffin or mixed-base crudes, but it has not been particularly satisfactory for California cracked gasolines. It is the author's opinion that the reason for this is the presence of the above mentioned hydrocarbons which act as catalysts for gum formation. These compounds are not removed by absorbents. Only di-olefins are removed by the aid of absorbents, but the catalyst-compounds remain unattached and pass with the gasoline vapors to the cooling system. Because of the characteristics of this catalyst to induce polymerization of the olefins during long standing, it is easy to understand that the quality of such gasoline will decrease in spite of its clay refining.

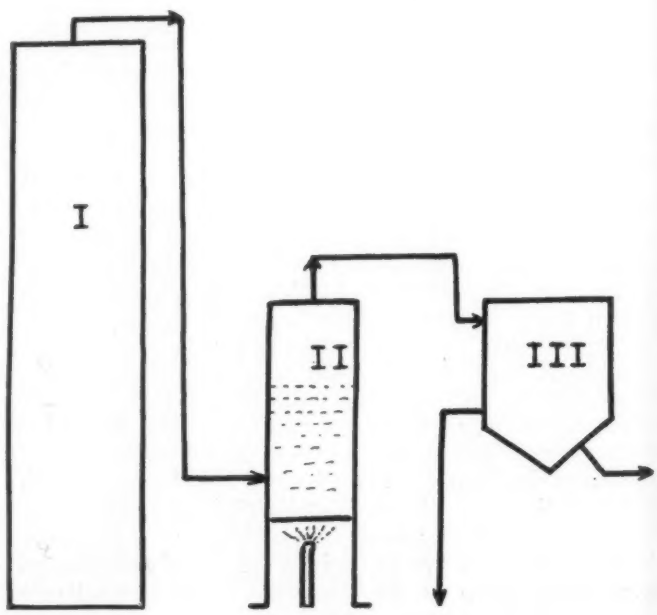


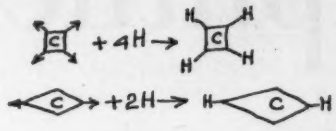
FIGURE 1

To remove these impurities the author has carried out the following experiment (Figure 1): The cracked gas from the bottom of the fractionation tower, I, was directed to a smaller tower, II, filled with a lubricating oil of about 3-4 degrees Engler at 100° C. This oil was heated by means of a burner, placed under the tower, heating it to a temperature of 300-350° C., in order to avoid the solution of the gasoline in the oil. It has been stated that the gasoline, after having passed through the oil, was free

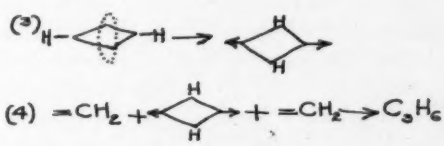
of the above-mentioned impurities. Such gasoline exposed to the action of sunlight (in bottles), and in the absence of oxygen, showed no change in color, nor any gum deposition; the impurities had been absorbed by the oil.

However, this gasoline contains a great deal of di-olefins, which are easily polymerized to gums. Therefore, the cracked gas after leaving the absorption tower is now directed to the clay treating tower, III, where polymerization of di-olefins takes place. Various absorbents have been reported as being suitable. The author has found that the natural bleaching clays are most suitable for this purpose. The artificially activated bleaching clays cannot be used for this purpose, since even small traces of any residual hydrochloric acid tend toward producing injurious hydrocarbons. It has been found and verified that hydrochloric acid or aluminum chloride, when existing in the sphere of action of a bleaching clay, show quite other characteristics than when these agents exist alone. These agents, when present merely as traces in the clay, cause certain hydrocarbons to split-up, forming an unknown compound soluble in the gasoline, this compound acting as a catalyst for gum-formation. This reaction takes place very slowly at first, and is then accelerated by the continued formation of the above compound. The theory is about as follows: Certain unsaturated hydrocarbons can be split-up by means of the combined ordinary action of a clay plus hydrochloric acid, or by the combination clay-aluminum chloride, into active unsaturated hydrocarbons. These highly active hydrocarbons are able to cause intermediate reactions not only with the unsaturated hydrocarbons but with aromatic hydrocarbons as well, the consequence being the polymerization and condensation between unsaturated and aromatic hydrocarbons. These reactions lead to a lowering of the antiknock value of the gasoline, since the unsaturated and cyclic hydrocarbons are removed as gums from the gasoline. Viewing these phenomena in the light of the above, we are forced to the conclusion that only natural clays are suitable for the contact refining of cracked gasolines.

Let us now consider the polymerization of gaseous hydrocarbons into gasoline-like hydrocarbons. The author has studied this problem quite a while, and has recently established the fact that even the decomposition and hydrogenation of hydrocarbons are nothing but the result of certain polymerization reactions. In other words, cracking, hydrogenation and polymerization are all derived from a first or fundamental reaction, which is the complete splitting-up of hydrocarbons into free carbon and hydrogen. In the first phase, the carbon and hydrogen exist in statu nascendi. Carbon cannot be obtained in this form, as it is only in a potential state. It exists in this form a very short length of time under certain conditions, since it possesses the tendency to "absorb" some potential atoms of hydrogen. According to observations of the author two sorts of potential carbon can exist in the first phase: the carbon with four free linkages and the carbon with two free linkages. According to these structures, the first form of carbon is able to combine with four atoms of hydrogen, while the second form combines in the first phase with only two atoms of hydrogen:



The first reaction shows that methane can be produced under certain conditions, but leading to no desired aim. Moreover, the hundred percent formation of this compound requires very high temperatures, pressures, and especially long reaction times, a phenomenon which is observed in a nature in the formation of natural gas. The second reaction during the decomposition or cracking of the hydrocarbons is the formation of $=CH_2$ molecules. At the moment of formation of this potential molecule, that is, at the moment of saturation of two mutual free linkages, these points will be pressed in such a manner that the structure will be changed, the consequence being the activation of the other two linkages. Reaction 3:



This new structure combines with the free linkages of two $=CH_2$ molecules, as indicated in reaction 4, the latter being an ordinary polymerization reaction. This structure can also combine under certain conditions, instead of the two $=CH_2$ molecules; with two atoms of hydrogen. This reaction leads to saturation of the polymerized hydrocarbons. The effect of temperature here is very great, not so much because of differences produced in the properties of the gasoline, but because the high temperature changes the direction of the polymerization. Furthermore, pressure also influences the polymerization of these $=CH_2$ molecules. With increasing temperatures and pressures, the chain of hydrocarbons produced will be longer. Of course this polymerization is influenced by the type of oil used in the cracking, and by the content of available hydrogen in the oil. Since the oil contains on the average some 15 percent of hydrogen, a great quantity of free carbon in statu nascendi remains uncombined by hydrogen atoms.

A large part of these carbon atoms is forced to combine between themselves as follows:

$$—C— + —C— + —C— \rightarrow —C—C—C—$$

This reaction leads to the formation of higher molecular weight hydrocarbons; however, not all the free carbon is able to enter into this reaction. The result is the disappearance of its activity, leading to the formation of coke. A part of the free carbon with two active linkages will be transformed, under certain temperature and pressure conditions into carbon with four active linkages. Since a 100 percent formation of methane from these carbon atoms cannot be easily accomplished, their activity disappears in a short time, with coke formations as a result. On the other hand, the methane will be split up into carbon and four atoms of hydrogen. Under

[*Continued on page 77*]

Naphthenic Acids

Direct from

Crude Oils

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RECOVERY of naphthenic acids as a by-product of petroleum refining operations has steadily increased in importance since its inception in Russia towards the end of last century. For many years the principal source of these acids was the alkali residue from the refining of kerosene in European refineries, principally in Russia and Roumania. Recently, however, owing to the greatly increased industrial outlet for naphthenic acids, the attention of American refiners has also been turned toward the production of this valuable subsidiary product. In practically all of the published processes for the recovery of naphthenic acids these latter have been obtained from petroleum distillates, and very largely from light distillates such as kerosine and gas oil ("solar oil") in which these acids tend to concentrate. In former times almost the only source commercially available was the alkaline refining residues of kerosene, and in some cases also, of spindle oil. Recently, according to Shipp,[1] the combined effect of increasing demand for these acids and the growing importance of the gas oil fraction as a fuel for compression-ignition engines has led to some refineries adopting the practice of washing the gas oil with a weak caustic soda solution and extracting the naphthenic acids from the resultant aqueous soap solution. Thus, in addition to increasing the production of naphthenic acids by a relatively simple and cheap refining operation the quality of the gas oil as a Diesel fuel is considerably improved, since it is generally recognized that an appreciable organic acidity is an undesirable feature of such a product.

Whereas considerable attention has been paid to the recovery of naphthenic acids from various petroleum distillates there has been available very little data on the utilization of crude oil itself, prior to distillation, as a source of these products. While it is generally agreed that the removal of naphthenic acids from the crude oil would be a desirable procedure from the point of view of improving the quality of the subsequent distillates, and rendering them considerably easier to refine, to say nothing of the incidental value of the acids so recovered, there seems to be a general impression that such a procedure is impracticable on account of the formation of persistent emulsions of crude and soda solution which would lead to considerable difficulties in the subsequent handling of the oil. While doubtless this is true of a great number of crude oils it has however been found that, in the case of certain light crudes, treatment with alkaline solutions prior to distillation can be successfully carried out on a works scale. A large number of the processes suggested for the pre-treatment of crude oil do not include any provision for the recovery of the naphthenic acids so removed. Many of them consist of various methods of distilling the crude over alkali, and, in many cases, subjecting the residue (containing the naphthenic acids in combination with the alkali, together with any excess alkali) to cracking.

Schmitz,[2] in a discussion of the subject in which he strongly advocates pre-neutralization as being of considerable assistance in the subsequent treatment of the distillates, does not give any actual results obtained by the alkali-washing of crude oil (which he appears to consider more of a theoretical desideratum than a practical possibility) and confines himself to discussing the effects obtained by the neutralization of various distillates prior to their being refined. The only reference dealing with the pre-neutralization of crude oil, combined with the recovery of naphthenic acids from the alkaline extract of the crude, which the writer has been able to find in recent literature is to the work of Velikovskii and Druzhina,[3] to whose interesting results further attention will be drawn.

PRE-NEUTRALIZATION OF PERUVIAN CRUDE OIL

Work recently carried out at an English refinery, operating on a light Peruvian crude oil, has shown that the washing of this crude, prior to distillation, with a caustic soda solution and subsequent separation of the alkaline extract for recovery of the naphthenic acids contained therein, is a perfectly practicable procedure and such treatment has now become routine practice.

The crude oil to which this process is applied is obtained from Peru and has the following approximate characteristics:

Spec. Grav. at 60° F.	0.8475
Acidity (Mgm. KOH per gram oil)	0.65
Sulphur	0.07%
Redwood I viscosity at 32° F.	52″
Redwood I viscosity at 70° F.	40″
Distillation (Preliminary, I.P.T. method C.P. 3., 1935)	
I.B.P.	67° C.
Percent volatile at 75° C.	2
Percent volatile at 100° C.	5
Percent volatile at 125° C.	14
Percent volatile at 150° C.	25
Percent volatile at 175° C.	32
Percent volatile at 200° C.	38
Percent volatile at 225° C.	45
Percent volatile at 250° C.	50
Percent volatile at 275° C.	56
Percent volatile at 300° C.	63

INTEREST lately has been re-awakened in the recovery of naphthenic acids from petroleum. By far the greater part of the naphthenic acids described hitherto have been obtained from various petroleum distillates, and the use of crude oil as a direct source of such acids has been largely neglected. Despite a general impression that the recovery of naphthenic acids from crude oil, prior to the distillation of the latter, is an impracticable procedure, such is by no means always the case.

Apart from the improved distillates obtainable as the result of such a removal of naphthenic acids, the acids themselves form a valuable product of ever-increasing industrial importance. Methods for the refining of such acids have been evolved and proved satisfactory on a plant scale.

The similarity of naphthenic acids obtained from Peruvian crude oil to those recovered from Russian crude is noteworthy.

The crude is classed as "naphthene-intermediate wax-free" according to the U. S. Bureau of Mines method for the classification of crude oils; it is processed in a two-stage distillation unit of which a description has already been published in this journal.[4]

Although the crude is by no means an exceptionally rich one as regards its naphthenic acid content (approximately 0.3 percent) the acidities of the distillates from untreated crude oil are by no means negligible, as will be seen from Table I, where there are also given the acidities of the same products when recovered from alkali-washed crude.

TABLE 1

Acidities of distillates from unwashed and from washed crude.

PRODUCT	ACIDITY (Mgm. KOH/gm.)	
	From Unwashed Crude	From Washed Crude*
Gasoline (end-point 175° C.)	0.02	Nil
Kerosene (175° C.–260° C.)	0.07	Nil
Gas Oil (260° C.–380° C.)	2.35	0.06
Spindle Oil (Red. I visc. @ 70° F. =140″)	1.40	0.27
Light Engine Oil (Red. I visc. @ 140° F. =98″)	0.95	0.05
Heavy Engine Oil (Red. I visc. @ 200° F. =82″)	0.60	0.04
Cylinder Stock (Red. I visc. @ 200° F. =200″)	0.30	0.04
Bitumen (Penetration =180/200)	0.30	0.04

* It is interesting to note that the acidity of the spindle oil is not brought down as much as that of the more acid gas oil; this shows that the low molecular weight acids present in the latter fraction have a considerably greater affinity for the alkali than the heavier acids corresponding to the spindle oil range.

It will be seen from Table I that the acidities of products recovered from untreated crude oil, while appreciable, are by no means outside the usual range of figures recorded for similar products. Nevertheless, it is a generally recognized fact that the lower the acidity of a distillate the more satisfactory it is from several standpoints.

Laboratory experiments were therefore initiated on the reduction of the acidity of the crude oil by treatment with caustic soda. It was found that, by this means, the acidity of the crude oil could be brought down from the original figure of 0.65 to a value of 0.09. After the laboratory experiments had been satisfactorily completed large scale processing was begun and has since completely justified itself.

RECOVERY OF THE NAPHTHENIC ACIDS FROM THE ALKALINE EXTRACT OF THE CRUDE OIL

The alkaline extract of the crude oil, which is in fact a dilute solution of sodium naphthenate, is transferred to a separate treating tank where the naphthenic acids are recovered. This recovery is accomplished in the usual manner by the decomposition of the soap solution with sulphuric acid, which has the effect of forming sodium sulphate which dissolves in the aqueous layer and liberating free naphthenic acids, which float on the top of the liquid and they are removed and transferred to storage.

The naphthenic acids obtained in this manner contain up to 5 percent of water; if a drier product is required the tank in which the acids are held should be heated to about 180/200° F. and settling allowed for a few days, by this means naphthenic acids with a water content of ½ percent or less are easily obtainable.

The naphthenic acids thus recovered are dark brown to black in color, with a characteristic odor, and an analysis of which the following is typical:

TABLE 2

Unrefined naphthenic acids as recovered direct from crude oil.

Spec. Grav. at 60° F	0.973
Acid value (Mg. KOH/gm.)	155
Water	0.5%
Engler Viscosity at 50° C	9.14
Flashpoint, open	84° C.
Cold test	Fluid at 0° F.
Sulphur	0.13%
Ash (largely iron oxide)	0.11%
Unsaponifiable matter	26.3%
Acid value of pure acids	210

The amount of acids recovered in this manner amounts to about 0.25 percent of the crude oil treated and is thus about 80 percent of the amount of naphthenic acids originally present in the crude oil. (This latter figure, given above as 0.3 percent, was calculated from the ratio of the acidity of the crude oil (0.65) to that of the pure acids extracted from the crude acids recovered as above (210).

THE REFINING OF THE CRUDE NAPHTHENIC ACIDS

Although the acids obtained in the above manner compare not unfavorably with many of the grades on the European market it was however desired to produce a better quality of product if this was economically possible. With this end in view several methods of improving both the color and the acid value of the naphthenic acids were investigated.

The first method tried was to treat the naphthenic acids as though they were an unrefined lubricating oil and to attempt to refine them in the classical manner with sulphuric acid (or oleum) and bleaching earths. Only by the use of drastic quantities of acid was there any appreciable improvement in the acid value of the acids and even then the appearance was barely affected. In addition, the separation of the acid sludge was accompanied by such difficulties as

to make the method obviously impracticable. Recent methods described in the literature[5, 6] suggest the treating of naphthenic acids in gasoline solution with sulphuric acid so as to enable the removal of the acid sludge to be more easily accomplished; despite optimistic claims by the authors of these methods they were found to be totally inapplicable to the crude naphthenic acids produced in the above-described manner. Clay treatment alone of the acids and also clay treatment of the alkaline crude extract prior to acidification were also tried but proved unavailing.

Other methods investigated were the fractional acidification of the alkaline extract so as to precipitate, first the resinous bodies present and the naphthenic acids of high molecular weight (and therefore of low acid value) and, subsequently the naphthenic acids of low molecular weight (and conversely of high acid value). While the product obtained in this manner was of quite good quality, the yield was so small as to make the method inapplicable to commercial operation.

The converse of this method, namely the extraction of the crude naphthenic acids with a weak caustic soda solution containing insufficient alkali completely to neutralize the acids was also found to suffer from the same disadvantage.

The method which was finally found to be satisfactory and which, when applied on a works scale has proved highly successful is that of steam distillation.

The crude acids described above are placed in a small batch still and distilled with the aid of superheated exhaust steam. The still is oil-fired. The distillation proceeds with extreme smoothness and the control of the distillation is carried out on information derived from the periodic determinations of the acid value of the distillate which are carried out by the laboratory.

As will be seen from the data given above the crude naphthenic acids contain over 26 percent of unsaponifiable matter. This unsaponifiable matter is in fact crude oil which has dissolved in the alkaline solution (it is a well known fact that aqueous solutions of sodium naphthenate possess appreciable solvent power with respect to mineral oil) and which is liberated on the acidification of the alkaline crude oil extract and is thereby mixed with the naphthenic acids. It will be seen from Table 1 that in the distillates produced from un-neutralized crude oil there is no appreciable amount of naphthenic acids until the gas oil cut is reached; similarly it will be seen from the characteristics of the crude oil, as given above, that over 50 percent is volatile up to the beginning of the gas oil range.

Hence it should follow that the distillation of the crude naphthenic acid mixture up to a temperature in the region of 260° C. should eliminate a large proportion of the unsaponifiable matter without any great loss of naphthenic acids. In actual practice this is found to be the case; the method of operation of the naphthenic acid still is to start distillation and carry on until a sharp increase in the acid value of the distillate commences, the stream is then switched to another receiver and the distillation continued until, the acid value having passed its peak (which is a figure somewhere in excess of 200), begins to fall off. Soon after this point, depending upon the desired acid value of the product, the distillation is stopped.

The temperature at which the distillation begins is about 150° C. (overhead) and it rises slowly to about 280° C. The maximum bottom temperature attained is approximately 350° C.

The amount of steam used in the distillation is considerable and the quantity of water condensed with the naphthenic acids may amount to 30/40 percent of the naphthenic acid distillate. No difficulty whatever is experienced in separating the water and acid layers; this separation is however speeded-up and rendered sharper if the receiving tank is heated, say to 160° F.

The refining of naphthenic acids by steam distillation results therefore in the formation of three products.

A. A light cut, consisting principally of unsaponifiable matter and which is, in practice, returned to crude oil.

B. The main portion, consisting almost exclusively of naphthenic acids and towards whose separation the entire procedure is directed.

C. A hard bituminous residue which can be used for either of the following purposes:
   (i) As a hard grade of asphalt;
   (ii) As a base for a bituminous paint, the high resin content should be of advantage here.

It will thus be seen that the refining porcedure sonsists essentially in the removal of portions from the "head" and "tail" of the crude naphthenic acid mixture leaving the desirable middle portion. The "head" portion consists principally of light mineral oil (up to a very light gas oil in distillation range) together with a small quantity of high acid value naphthenic acids; the "tail" portion consists of the low acid value acids corresponding to the heavier lubricating oil and bitumen fractions of the crude oil and also of acidic resins which have been extracted from the crude oil by the caustic soda solution, and which, being non-volatile remain in the residue on distillation. These resinous bodies are presumably the material which is dropped out as acid sludge when the crude naphthenic acids are treated with sulphuric acid, hence the increase in the acid value of naphthenic acid so treated.

The following analyses of these fractions, obtained during a trial laboratory distillation, are typical and approximate very closely to those obtained from the plant.

FRACTION A—8.1 Percent (by weight):	
Spec. Grav. at 60° F.	0.827
Acid value (Mgm. KOH/gm.)	37
Unsaponifiable matter	87.7%
Acid value of pure acids	301
Distillation (I.P.T. method G.3, 1935)—	
I.B.P.	145° C.
Percent volatile at 200° C.	40
Percent volatile at 300° C.	85
F.B.P.	330° C.
FRACTION B—75.3 Percent (by weight):	
Spec. Grav. at 60° F.	0.976
Acid value	190
Unsaponifiable matter	15.6%
Acid value of pure acids	224
FRACTION C—16.6 Percent (by weight):	
Spec. Grav. at 60° F.	1.063
Acid value	52
Penetration (I.P.T. method, A.18, 100 gm. 77° F. 5")	8
Melting Point (Ring and Ball)	66° C.
Matter insoluble in CS_2	0.3%

The water that resulted from the condensation of the steam was separated and extracted with petroleum ether. This yielded about 0.1 percent (on the charge) of naphthenic acids with an acid value of 260. It may be remarked that the pure acids separated from fraction A possessed a very marked phenolic odor.

The starting material in the above experiment had the characteristics given in Table 2.

It will thus be seen that the naphthenic acids obtained from the crude oil are very largely volatile in steam; this is contrary to the statement made by Naptali[7] that they are only partially steam-volatile. The figure quoted by Naphtali for the acid value of the steam-volatile portion of naphthenic acids (of unstated origin) is 262, which corresponds to acids of a considerably lesser molecular weight than those which, judging by the acid value, are present in fraction B, above.

The distilled naphthenic acids (fraction B) obtained by the above method are of a dark red color and have considerably less odor than the crude acids. They may be considered as a high-grade product and have an unsaponifiable matter content considerably less than that of most naphthenic acids hitherto met with commercially. Their acid value is also less than that of products previously manufactured; this is due to the fact that these acids correspond to a very much wider fraction of crude oil than those formerly available, which as already mentioned, were obtained solely from light fractions and would, in consequence, have the low molecular weight (i.e. high acid value) of the acids that accompany such fractions. By contrast the acids obtained from crude oil include those corresponding to the medium lubricating oils (those corresponding to the heavier lubricating oils are, as stated above, left in the residue on steam-distillation) and which have moderately high molecular weights. In spite of the relatively high quality of the steam distilled acids it is required, for certain industrial purposes, to have naphthenic acids possessing a color equivalent to that of a pale red lubricating oil, or even better. To produce such grades the acids obtained by the method described above are further refined as follows:

The acids are washed with 10 percent of a weak (10 percent strength) sulphuric acid solution, this treatment is followed by a water wash to eliminate any mineral acid left after running off the sulphuric acid and, after removal of the water by settling, the acids are treated with a bleaching earth, any of the common commercial earths being employed for this purpose, and filtered through a filter press. The treatment with sulphuric acid and the subsequent water washing are carried out at temperatures in the neighborhood of 160° F., the clay treatment is carried out at 230° F., at which temperature any remaining traces of moisture are removed and a bright transparent product is yielded. No difficulty is experienced in settling off the sulphuric acid or the water after the respective treatments. These are carried out in a steam jacketed mechanically operated mixer. The amount of bleaching earth used varies from 2 percent to 5 percent (by weight), depending upon the color desired in the finished material.

The reason for the sulphuric acid wash in the above refining scheme is that, during the condensation of the hot naphthenic acid vapor following the distillation, the iron of which the condenser attached to the still is made, is attacked to a certain extent by the acids, as are also, but to a much lesser degree, the tanks in which it is settled hot, with the result that a dark-colored iron naphthenate is formed and dissolves in the acids. On treatment with weak sulphuric acid this iron soap is decomposed, regenerating the naphthenic acid it has absorbed and forming iron sulphate. This latter is then removed partially in the water used to wash the acids following the sulphuric acid treatment and partially by the filtration following the clay treatment. The amount of iron soap so formed is minute but nevertheless sufficient to affect noticeably the color of the distilled acids.

The final finished acids produced by this process test as follows:

Spec. Grav. at 60° F.	0.976
Flash point, open	140° C.
Engler viscosity at 50° C.	4.2°
Unsaponifiable matter	15.6%
Color (Lovibond tintometer, ¼" cell)	16Y/1.2R

It is of interest to note that the above described method for the refining of naphthenic acids, which was evolved independently by an English laboratory, is almost identical with that recently described by Goldberg and Kochoeva[8]. These authors also found that refining naphthenic acids by means of sulphuric acid was impracticable and they also could not repeat the results published by Liubarskii and Tiablikova[5] and by Rabinovitch and Osenova[6], who claim to have been successful in this respect.

The naphthenic acids used by Goldberg and Kochoeva had the following characteristics:

Acid value	188
Color (diluted 1:5 in Duboscq colorimeter)	3 mm.
Unsaponifiable matter	14%
Acid value of pure acids	219

They are thus seen to be very similar to the acids used as the basis of the English experiments. It is not stated whether the acids used by the Russian workers were obtained directly from crude oil or from petroleum distillates, the trend of recent Russian work, however, together with the characteristics of the acids suggests crude oil as their source.

By steam-distillation Goldberg and Kochoeva obtained a yield of 76 percent light colored distillate having an acid value of 239; the residue obtained by them was a pitch-like material with an acid value of 100. Similar to the effect mentioned above they also noticed the action of the distilled acids on the iron of the condenser and state that the discoloration of the distilled acids produced in this manner can be removed by treatment with weak sulphuric acid.*

It is of interest that they remark that the treatment of the crude acids (in gasoline solution) with clay alone does not yield satisfactory results; treatment with activated charcoal as the adsorbing agent was successful but the loss of acids by this method

* In their published work Goldberg and Kochoeva describe laboratory experiments only; they do not state whether the method has been transferred to a works scale. The pre-neutralization of crude oil described by Velikovskii and Druzhina has been operated on a plant scale as an experiment; they do not state whether it has become routine practice and their pre-neutralization seems to have required special precautions (such as heating the crude oil) to avoid emulsion-formation. Their distillation of naphthenic acids appears to relate to laboratory work only.

TABLE 3

Vacuum distillation of crude naphthenic acids from Peruvian crude oil.

CUT No.	Percent of Charge (By Weight)	Overhead Cutting Temp. ° C. (Approx.)	Specific Gravity @ 60° F.	Acid Value (Mgm. KOH/gm.)
1	2.1	55	0.788	0.56
2	2.2	64	0.819	3
3	2.3	81	0.848	12
4	2.5	107	0.887	83
5	2.7	122	0.938	206
6	2.4	130	0.958	241
7	2.7	137	0.968	248
8	2.7	143	0.974	247
9	2.8	147	0.979	247
10	2.5	152	0.980	241
11	2.9	155	0.980	240
12	2.2	158	0.987	240
13	3.2	162	0.987	232
14	2.5	166	0.989	226
15	3.1	170	0.989	226
16	2.4	175	0.988	221
17	2.5	178	0.988	212
18	2.8	182	0.988	205
19	2.6	186	0.987	201
20	2.8	190	0.987	196
21	2.6	193	0.987	193
22	2.8	195	0.986	185
23	2.8	198	0.983	175
24	2.8	201	0.982	166
25	2.5	205	0.981	160
26	2.7	208	0.981	154
27*	2.0	214	0.975	135
28	1.7	222	0.972	118
29	0.9	230	0.968	110

* The constants of cut 27 were obtained by interpolation as this fraction was accidentally lost before the specific gravity and acid value could be determined.

was such as to render this procedure completely unworkable.

FURTHER EXAMINATION OF THE CRUDE NAPHTHENIC ACIDS

In order to obtain a more comprehensive picture of the composition of the crude naphthenic acids forming the material recovered from the alkaline extracts of the crude oil, this material was subjected, in the laboratory, to vacuum distillation*.

The starting material was the same whose characteristics are given in Table 2; the still employed was a metal still of 5 litres capacity having a fractionating column 2 inches in diameter and 18 inches in height packed with aluminum cones. The vacuum employed was 4 mm. of mercury.

The results obtained are given in Table 3.

The above figures show clearly the sudden sharp rise in acid value occurring when the light unsaponifiable matter has been driven off, and the gradual falling off in acidity after the peak value corresponding to about the end of the gas oil fraction has been passed and the successive cuts of acid begin to correspond more and more to the heavier lubricating oil region.

The total distillate amounted to 72.7 percent with an average acid value of 183, if the first four cuts, which consist largely of unsaponifiable material, are excluded the distillate amounts to 63.6 percent with an acid value of 204.

The residue from this distillation, amounting to 27.3 percent, had the following characteristics:

Spec. Grav. at 60° F.	1.03
Acid value	40
Sulphur	0.43%
Asphaltenes (I.P.T. method, A. 12)	Nil
Penetration (100 gm. 77° F. 5″)	55
Melting Point (Ring and Ball)	48° C.
Matter insoluble in CS_2	0.4%
Unsaponifiable matter	71.9%
Acid value of pure acids	142

It is interesting to compare the above results with those obtained by Velikovskii and Druzhina[3]. These authors have published some experiments on the alkaline extraction of Caucasian crude oils prior to distillation; their general results and conclusions are very similar to those here described for Peruvian crude. In the case of the naphthenic acids examined by them their figures are of particular interest since they are one of the few published results dealing with naphthenic acids obtained directly from crude oil and not, as those the majority of workers have hitherto investigated, from petroleum distillates.

In Table 4 will be found the results obtained by Velikovskii and Druzhina and also those obtained from the acids of Peruvian origin and given above in Table 3 but re-grouped so as to show their similarity to those of the Russian investigators.

It will be seen from the above table that although the cuts taken were not quite the same in extent in the two cases, the results for the acid values and percentages of unsaponifiable matter show an interesting similarity. The figures on the first fraction and on the residue in each case are remarkable in view of their extremely close resemblance.

The distillation temperatures are also of the same order although not strictly comparable since the degree of vacuum employed was different in the two cases, being 7 mm. in the case of the Russian distillation and 4 mm. in the case of that carried out in England. This close likeness, which is also shown by the already quoted work of Goldberg and Kochoeva, between the results of investigations on naphthenic acids originating in the one case from Peruvian petroleum and in the other from Caucasian is not without interest, especially since, as far as the writer is aware, the naphthenic acids of Peruvian crude have not been previously mentioned in the literature.

It may be added that similar experiments have been carried out with crude oil originating in southern Ecuador and which is almost identical with that from Peru whose characteristics have been given

* Atmospheric distillation was tried but found impracticable as the high temperatures necessary caused decomposition of the naphthenic acids by decarboxylation, as was shown by the low acid values of the distillates obtained.

TABLE 4

Comparative results on the vacuum distillation of naphthenic acids obtained from Peruvian crude oil and from Caucasian crude oil

FRACTION		Percent of Starting Material		Acid Value of: Fraction		Acid Value of: Pure Acids*		Unsaponifiable Matter, Percent	
A.	B.	A.	B.	A.	B.	A.	B.	A.	B.
Starting Material	Starting Material	100	100	115	155	181	210	37.0	26.3
Cuts 1 to 141.5° C.	Cuts 1–4, 55–122° C.	10.7	9.1	38	27	325	310	91.4	91.7
Cut 2, 141.5–178° C.	Cuts 5–19, 122–190° C.	10.7	40.0	165	228	292	271	43.5	15.8
Cut 3, 178–214° C.	Cut 20–26, 190–214° C.	15.1	19.0	192	175	240	205	20.2	14.5
Cut 4, 214–250° C.	Cuts 28–29, 222–230° C.	16.5	2.6	167	117	192	178	15.9	34.3
Cut 5, 250–270° C	.....	15.0	.....	120	.....	157	.....	24.2	.....
Residue	Residue	29.1	27.3	43	40	114	142	63.0	71.9

* i. e. freed from unsaponifiable matter.
A. = Results obtained by Velikovskii and Druzhina on acids from Caucasian crude.
B. = Results obtained on acids from Peruvian crude.

previously; in the case of the naphthenic acids derived from this Ecuadorian crude no noticeable difference to the naphthenic acids from the corresponding Peruvian crude could be noticed.

SUMMARY

Both experimental and works procedure showing the practicability of the washing of crude oil with caustic soda solution is mentioned. Such treatment has the effect of considerably improving the quality of the distillates and of yielding naphthenic acids as a valuable by-product.

A practical method of refining these acids to yield a high grade product is described.

A preliminary examination of the crude naphthenic acids has been made and the results obtained compared with those published by other workers for naphthenic acids of Russian origin, which latter appear to resemble closely those from Peruvian crude oil.

ACKNOWLEDGMENT

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LITERATURE CITED

[1] Shipp, Oil and Gas Journal, 1936, (34), No. 44, 56.
[2] Schmitz, Erdol und Teer, 1932, (8), 27, 44.
[3] Velikovskii and Druzhina, Neftyanoe Khozaistvo, 1933, (25), 48.
[4] Altshuler, Refiner, 1935, (14), 140.
[5] Liubarskii and Tiablikova, Masloboino Zhirovoe Delo, 1934, No. 7, 30.
[6] Rabinovitch and Osenova, Masloboino Zhirovoe Delo, 1934, No. 12, 41.
[7] Naphtali, "Chemie, Technologie und Analyse der Naphthensauren," Stuttgart, 1977, p. 55". See also, "Naphthensauren und Naphthensulfosauren," Stuttgart, 1934, by the same author.
[8] Goldberg and Kochoeva, Masloboino Zhirovoe Delo, 1935, (11), 594.

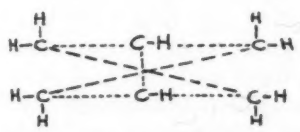
Polymerization

[*Continued from page 71*]

certain temperature and pressure conditions this carbon will be transformed into carbon with two active linkages. The remaining hydrogen atoms will be "absorbed" by two active linkages of unsaturated hydrocarbons, as follows:

(1) $CH_4 \rightarrow C + 4H$; (2) $C + 2H \rightarrow =CH_2$; (3) $C_3H_6 + 2H \rightarrow C_3H_8$.

When polymerizing $=CH_2$ molecules at high temperatures the active linkages will act in the middle of the three or more $=CH_2$ molecules, as indicated below:



The result is that with increasing temperature and lowering of the pressure, the mutual active linkages of the polymerized $=CH_2$ molecules will enlarge their activity, having as a consequence the formation of cyclic hydrocarbons. Therefore, it is necessary to be able to guide one of the two reactions indicated by the hypothesis. For this purpose a proper catalyst must be used, since it must be able to regulate the entry of hydrogen in the active carbon. Of course a proper catalyst may also transform the carbon with four active linkages into carbon with two active linkages. Simultaneously with the polymerization reactions, sulphur, nitrogen and oxygen compounds undergo the same reaction. In the first phase these compounds will be split-up into free active sulphur, nitrogen and oxygen, and in the second phase transformed into hydrogen sulphide, ammonia and water. That is why the polymer distillates are lower in sulphur content than the cracked gasoline where the process in the first phase is not complete due to unfavorable conditions.

It follows from the above, that the formation of the four groups of hydrocarbons, namely, unsaturated, naphthenic, aromatic and paraffinic hydrocarbons are the result of different reaction-movement of the $=CH_2$ molecules, and whose composition varies as a function of temperature, pressure and time. In other words, in order to produce a high antiknock gasoline, it is necessary to operate under proper temperature-pressure conditions. The molecular weight of the constituents also influences the polymerization of hydrocarbons.

As mentioned above, petroleum oils contain about fifteen percent of available hydrogen, which makes impossible the complete transformation of the higher molecular weight oils into the lower hydrocarbons since a great quantity of active carbon is unattached by hydrogen. Therefore a great part of these carbon atoms are forced to combine among themselves. This reaction leads to the formation of higher molecular weight hydrocarbons. On the other hand, many carbon atoms lose their activity and precipitate as coke. In order to avoid these sort of reactions, the hydrogenation process is used. This process consists of the addition and action of compressed hydrogen on the split-up carbon atoms. Viewing the hydrogenation process in the light of the above considerations, we are forced to the conclusion that it is nothing but the artificial supply of hydrogen in the reaction chamber to increase the production of the $=CH_2$ molecules.

SUMMARY

The above considerations and theories indicated show that the phenomena of "polymerization" play the most important part in all branches of the oil-refining industry. However, it must be stated that the polymerization shows different characteristics in each refining branch. For instance, the polymerization in the distillation process and refining with the aid of sulphuric acid may be considered as a very undesirable process, whereas the exact polymerization of $=CH_2$ molecules into gasoline presents a most convenient and economic process for the refining industry. Polymerization should be considered as the most important factor in refining processes, and therefore the aim of the petroleum technologist should be the ability to discriminate between the desirable and undesirable reactions.

REFERENCES

[1] Refiner & Natural Gasoline Man. No. 4, p. 88-89; 1928.
[2] Jour. Soc. Chem. Indust, 863, 1928.

Design Features of Canfield's New Filtration Plant

AFTER a fire destroyed Canfield Oil Company's filter plant at Coraopolis, Pennsylvania, in June, 1935, it was necessary to rebuild the plant with as little loss of time as possible. The plant which was destroyed was more or less obsolete, but still was capable of processing a satisfactory amount of oil. The company engineers had made tentative plans for a new plant, and had investigated the desirable features of newer and more modern filtration plants, and therefore, only six weeks elapsed between the time of the fire and when the new plant was in operation, turning out a larger quantity of oil in less time and with less cost than had the old plant.

The new unit is housed in a brick and concrete building on the street facing the refinery office, it consists of three floors and an elevator shaft to connect it with the clay burning unit next door. The first floor contains the circulating and charging pumps together with the instruments for control of the processes. Directly under the eight filter-clay vessels is the clay-handling machinery with facilities which dump the filters and moves the spent clay by belts directly to the hopper above the burning furnace in straight-line flow. One section of the first floor is the filter operators' control room, with pressure gauges, flow meters and sight glasses so the operator can always determine the color of the oil flowing from the filters.

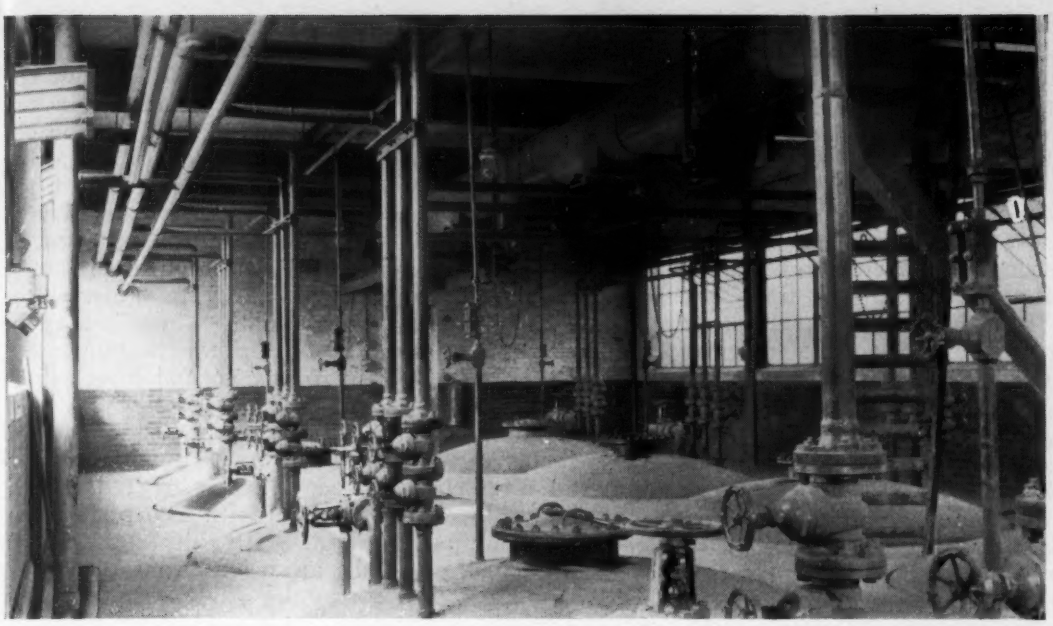
The second floor is devoted entirely to filter vessels. No openings other than those necessary were built into the walls of this room, and what are there are always closed, so as to conserve the heat of filtration in order to obtain a more even flow of oil through the beds of clay. The upper heads of the eight filters are almost flush with the floor of the third story of the building, and the lower conical ends protrude slightly through the ceiling of the first floor. Thus, the bodies of the filters are covered by the space occupied by the second story of the plant.

The filter vessels are 9 feet in diameter by 18 feet in length, with the filling manholes in the center of the upper ends. The manholes are standard as to type, and are fitted with two handling bails so that they can easily be removed. All of the oil and steaming lines installed to serve the filters are placed off center, on the wall side of the vessels. With the service piping placed in the heads of the filters on the wall side of the building, lighting is directly upon the valves.

All lines entering and leaving the filters, at whatever point they are installed are equipped with double valves, one above the other for positive shut-off. When a filter has been filled with clay preparatory to running oil, each valve on the individual line which is in service is opened. Both valves are always opened at the same time and closed when the line is cut from service. In this way, all valves are known to be in working order and not sticking. These valves are all equipped with flanged ends for ease in removing, and if one is closed, but does not shut off the flow of liquid, the other one is closed also, which prevents the flow of oil. The one found to be in bad order is immediately removed and replaced with a new valve.

It was desired to install piping throughout the filter plant without threads and couplings, so each joint was welded to the other, and welding flanges were used where gates were to be placed for control. All piping serving the top of the filters is arranged and supported above the eight units so that nothing is in the way of men when filling a filter with fresh clay, or inspecting the process while in service. Where a number of lines rise from the head of the filter, they are tied together with braces to minimize vibration. Pieces of angle irons having the required length to pass from each outer line is used as braces and "U" bolts secure the piping to the angle iron. All connections which required manipulation, such as gate valves and the like, are installed in the lines at the proper height from the floor of the rooms so that an operator can open or close them, or otherwise handle them without stooping, or reaching above the most convenient point.

The filter vessels, equipped with conical bottoms, have the oil lines installed at the tip of the inverted cones, so that all oil can run from the vessels to the pumps or tankage. The manholes through which the spent clay is removed are in the side of the cone, having been installed in that position to facilitate the removal of clay, and to prevent disturbance of the oil lines. To prevent clay from travelling downward into the oil-removal lines, a non-corrosive screen was placed inside the vessel, on an angle not quite so steep as the sides of the cone. The screens are installed so the upper surface is flush with the lower side of the manhole opening, and sloping back and upward to be securely fastened to the interior at the base of the inverted cone. The slope which these screens have was determined from observations carried on in other filter plants, and are installed in this manner to facilitate the removal of spent clay without it packing against the sides and requiring the use of shovels or other instruments to break the packed base. As the filter vessels are in-



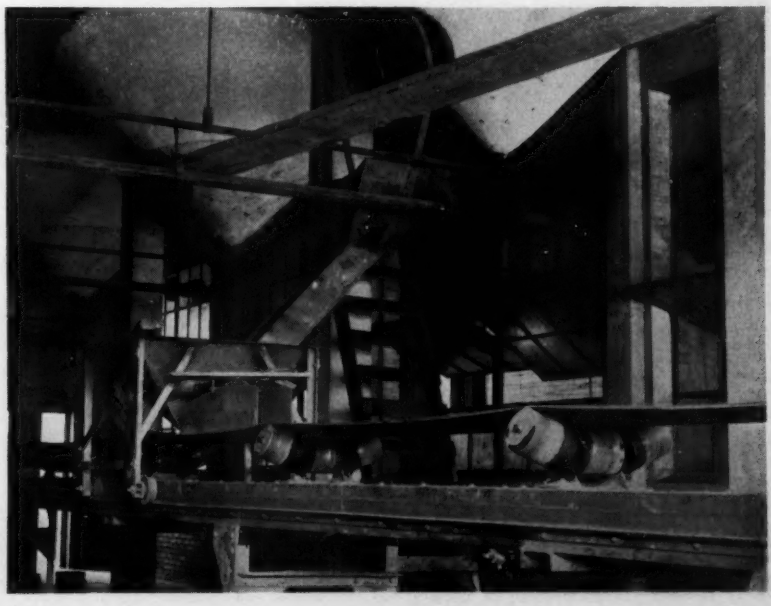
Top of Canfield's new filters at Coraopolis showing double gates on each line to control flow of oils should one gate fail.

stalled in two rows, each having eight filters, the manholes in each row faces those on the opposite side, which also provides ease in dumping, so that a single belt may serve each battery of filters.

Endless belts are employed to handle the spent clay. They extend from one end of the room to the other. When removing the spent clay from any of the vessels, it is gradually dumped upon the belt through a portable and mobile hopper. This belt and track for the hopper runs through the center of the room, and to direct the spent clay into the hopper, an extension funnel-like piece of equipment is employed which may be handled easily, and moved from one vessel to another, or, swung across the belt so as to service the opposite battery of filters. After the filter which is to be emptied has been placed in condition to remove the spent clay, the hopper is rolled to a point over the belt where it is under the manhole of the vessel. The funnel extension is placed directly under the manhole and supported by a bail which hooks over the hinge of the manhole cover. The bolts are removed which permits manipulation of the manhole cover so that the clay will spill out in a steady stream sufficient to load the belt evenly.

The clay upon the belt is moved to the end of the building where it empties upon the second conveyor which directs it to the elevator receptacle so the buckets may move it to the top of the building. The elevator leads from the side of the filter house directly to a chute which delivers the spent clay to the top of the clay burner. Electric motors are used to move the belts and conveyor buckets, the speed being controlled so a steady travel is obtained without piling up or spilling the clay over the sides of the conveyor belts. The motor used in driving the conveyor belts is only a 5-horsepower machine, transmitting power to the belt pulleys through a 28:1 speed-reducing unit. This is equipped with a pulley on one end of a shaft that drives the conveyor belt running through the room beneath the conical bottoms of the clay vessels, and a sprocket on a cross shaft which, through a chain, drives the belt leading to the elevator hopper.

Reconditioned clay leaving the burner is handled with an elevator which lifts the clay from the base to the top of the filter house building to a storage bin placed on the roof. The clay in the bin is reserve material, used for filling a filter after it has been cleaned of the spent clay. The base of the storage bin was placed sufficiently high that clay may be moved from it to a screw conveyor which runs the full length of the third story of the filterhouse, so that any filter may be charged. Four places were made in the screw conveyor shell where clay may be removed. A spout which was manufactured to hook below these takeoff boxes will swing from one filter to another opposite, with the discharge end lying over the top manhole so that clay may be placed where it is needed without being shoveled or otherwise handled. This screw conveyor extends be-



Filter dumping arrangement showing conveyor belt used to remove saturated clay from filters to burning unit.

yond the roof of the filterhouse so that clay which should be discarded after serving its purpose, can be moved to waiting trucks in the alley behind the canning and packaging room. Being reversible, this conveyor, also equipped with a bucket elevator which may be connected to the outer end, is also used when unloading cars of fresh clay. The cars when received are unloaded directly into the lower hopper of the bucket elevator by shoveling the clay from the cars, or emptying sacks with hand labor. This part of handling the clay is the only time that men are needed while it is in the plant, all other movements, from filters to burner, and back again, finally to the trucks for discarding are made with machinery.

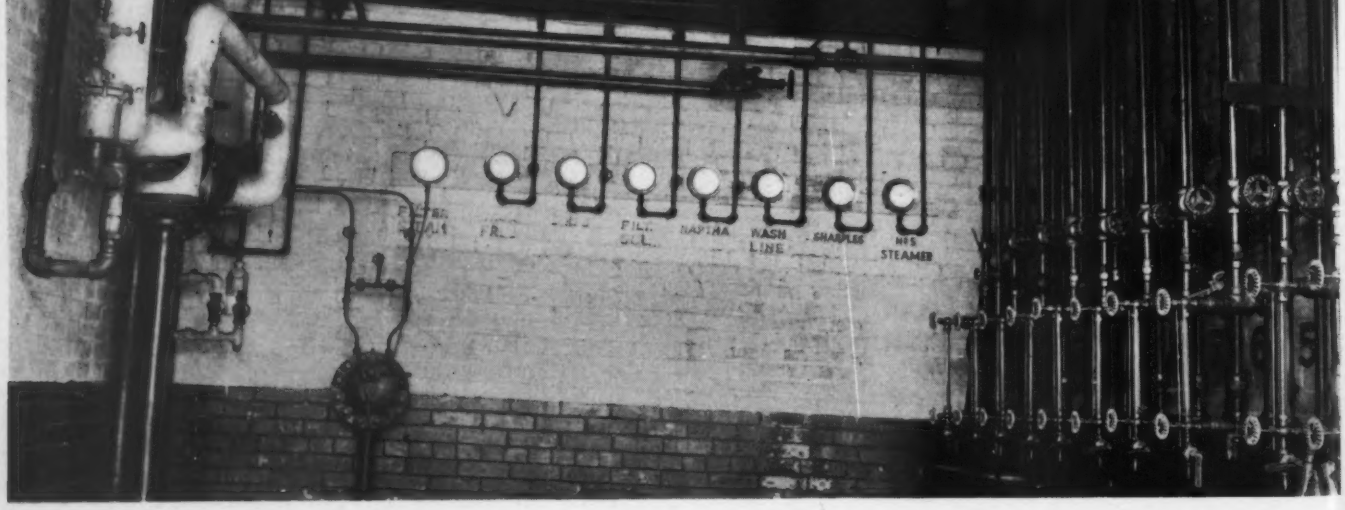
The steam pumps which handle the oil are in a room separated from other equipment by brick and concrete walls, equipped with windows which fill the outer wall so that the maximum amount of natural light may be had. Each pump is equipped with double instrument control, the controlling instrument being placed in the discharge lines of the pump, while the controller valve is installed on the steam lines. One of the instruments is what is called the "high pressure" controller, and acts instantly by shutting down the pump should the discharge pressure exceed a predetermined amount. The other, the "low pressure" controller acts instantly should the discharge pressure fall radically below the normal working pressure under which the pump is set. These two instruments are safety devices which not only protect workmen, but by acting instantly, prevent the loss of materia[1]. The high pressure anticipated may be caused from a valve being closed against the stream of oil being handled by the pump, and the low pressure from a broken pipe, or any other failure of equipment which would cause a sudden lowering of pump pressure.

The sampling room was placed in the corner of the building nearest the street and plant office entrance, for convenience, and contains the sight glasses through which a portion of the streams is always flowing so that the operator can easily tell what any particular filter is doing. Indicating pressure gauges were installed against the wall in the end of the building, opposite the windows in the front so a maximum amount of lighting may be obtained without resorting to artificial illumination. The sight feed, or stream indicating glasses, are fitted with sample cocks so a sample of the stream may be obtained at any time for determination of color. A catch basin, or sink was placed beneath these sample cocks and equipped with an adequate drain which allows waste oil to flow to a sump where it may be gathered up and pumped to slop for rerunning, or, it may be charged again to any special filter which may be running a particular grade of oil.

The amount of earth which may be charged to the unit when freshly filled is about 200 tons. A special grade of filter clay is used, which is treated to permit a longer life of the material with a corresponding greater throughput per ton. With this kind of filter clays used in the vessels, anywhere from 700,000 to 800,000 gallons of oil may be passed through the plant during any month, using a 50/50 solution, naphtha and oil. Because of the design of the filterhouse and equipment used, the capacity of this unit is about twice as great as the old one which it replaces. The cost of filtering the oil to any desired color is correspondingly reduced, because of the greater capacity, and because of the facilities for rapid charging, discharging and final disposition of discarded clays.

Oil flows through the pumps from the base of any filter vessel, or combination of vessels, as the case may be, directly to the stills where the lighter petroleum fractions are removed, using equipment formerly built for this purpose. From storage tanks, the finished oils, after blending to the required S.A.E. grades are pumped back to the new plant, which contains the packaging equipment, where it is placed in the desired type of containers. Being situated against the railroad switch which serves the plant as a whole, cased and barreled oils are placed in cars for final shipment. Throughout the entire plant, filterhouse and packaging room, the oil flows in a straight line from manufacture to final loading without the need of manual handling.

Control room of Canfield's filterhouse in Coraopolis, Pennsylvania, showing sight feed from filters to pumps, pressure gauges and constant color sample behind pair of lights in left hand corner.



Relation Between Refinery Departments and

The Laboratory

GEORGE F. FITZGERALD
Socony-Vacuum Oil Company

IN any active refinery the primary concern of everyone is to handle all the business it is possible to get. Every effort is made to fill customers' orders and maintain necessary stocks. These twin objectives are more often than not considered the only important ones. In the daily rush of handling regular business they are kept constantly in sight to the detriment of other important but somewhat minor matters. A particularly neglected point is often that of maintaining proper relations between departments.

It is inevitable that in an organization composed of interdependent departments friction will develop. The reasons for discord vary with the location and size of the plant and the nature of the business. Any part of the concern which has had its schedule upset by some other unit feels that it has a just grievance. If the delay has been caused by a laboratory rejection there arises more than the usual outcry. In many refineries there have been feuds of long standing between certain departments and the control laboratory. Disputes have arisen for various causes and possibly very little has been done to locate the basic problems. The resentment engendered by verbal battles is allowed to smoulder and each party remains convinced that he has been wronged. As time goes on the feeling becomes such that any plausible excuse is sufficient for making formal complaint.

One department will swear hoarsely that it is impossible to get any service on their samples without waiting hours. Another will say with great positiveness that the laboratory is inaccurate because as many as five different results were reported on the same batch of oil. The barrel house may argue that a certain one-barrel order must have been correctly filled because the oil came from a tank which had been approved by the laboratory. The oil inspectors may complain that much valuable time is lost when wax and petrolatum samples without instructions; that most samples are not truly representative.

In order to get at the truth of the situation and to do justice it is essential to get all the evidence. The laboratory can show that hours are actually required for such tests as pour, specific resistance, and penetration; that they often take full tests on a sample and then learn hours later that viscosity only was desired. On the other hand some special test, e.g. demulsibility or carbon residue, is required on a 7 a. m. sample but word to that effect fails to get around until shortly before quitting time. Much of the trouble arising from shipments of one barrel and less has been caused by transferring good oil through lines or pumps not thoroughly displaced.

A great deal of friction may be the result of error or neglect in the laboratory as well as out of it. Personnel in some laboratories adopt a discourteous or arbitrary manner in reporting to the plant. This attitude has a very undesirable influence on the way in which their reports are received. For example, many foremen have a feeling that an adverse report on their oil is a personal affront and the irritating voice makes him react accordingly. Others immediately ascribe the error to laboratory technique because nothing could be wrong with their oil. A little study will reveal that the old, experienced compounder resents being told by a youngster that his batch is not properly blended to viscosity. The veteran is positive that he is right because he followed the routine of years; the lad is equally sure he is right because his meter is standardized, his watch is calibrated and his technique is faultless. Where supervision is lacking such differences lead to the disputes which are the root of many charges against the laboratory. Furthermore, if the batch is again agitated and sampled until finally the proper viscosity has been reached the blender feels vindicated and forever after is convinced that the laboratory discovered its own mistake. (He overlooks the potent effect of further blowing. This point is not so weak as it may appear for the dispute just mentioned most often occurs when small batches are compounded in relatively large, flat-bottomed tanks. Under such conditions the shallow depth of oil will not become thoroughly mixed in the time usually allotted larger batches.)

Much of this interdepartmental friction is due to an incomplete understanding of the true function of the routine testing laboratory. To begin with, the position of the control laboratory should be exactly defined. Is it really to exercise control by enforcing specifications and rejecting all offtest material? Or is it to act merely as a fact-finding agency to collect data of no particular value except for filling blanks on printed forms? The choice between these definitions is all-important. The compromise stand of sometimes one and sometimes the other is so obviously unworkable that no comment is needed.

The laboratory logically should be expected to exercise control by detecting and reporting all deviations from standard. In order to do this, representative samples should be checked as early as possible in the sequence of refining operations. Obviously corrections can be much better made on semi-finished stock rather than in the loading tank just before shipping. Solution stills furnish a typical case. If they are allowed to run too light in viscosity with the vague intention of running heavier later on, the storage tank may be filled or the solution exhausted before a good average is obtained. Then there is no chance for adjustment and the laboratory is held responsible for allowing off-specification stocks to accumulate.

Next, the responsibility and supervision of the labora-

tory should be clearly established. Are the inspectors subject to the authority of all plant foremen and department heads? Is there an official head of the laboratory who reports directly to the plant manager? Is he to be governed by the arguments or opinions of department heads? Does he exercise personal supervision over control testing? Do other foremen encroach on his authority by attempting to direct their own samples through the laboratory?

A study of these questions will reveal many unsuspected causes of friction. A laboratory worker who is constantly harassed by three or four men with conflicting claims on his time finds it difficult to satisfy any of them. If his chief is not sure of his own status he is in no position to cope with other foremen. If the findings of the inspectors are subject to discount or dispute on the part of plant supervisors, then it is apparent that management has given scant thought to a definite policy of standards and tests.

There are in many plants foremen who made their start or at least had some experience in laboratory work. At first glance it might appear that such a condition would tend toward closer cooperation. On the contrary these same men are apt to cause the greatest interference and friction. They will think their inside knowledge justifies them in giving orders direct to inspectors and chemists and in ignoring or opposing those in charge. Frequently they will take it upon themselves to reprimand laboratory workers for real or fancied defects in their technique. These gratuitous "corrections" more often than not reveal how much the individual has forgotten or has failed to keep up with changes in methods and instruments.

INTERFERENCE WITH WORK

Where the plant men have the habit of running in to check up on the progress of their samples the laboratory may gradually be taken as a convenient meeting place for officials and foremen. There they confer on present operations and plan the future . . . usually in the center of the busiest working area. Of course it is possible for the inspectors to walk through and around these groups but it wastes time. In addition the distraction caused by such conferences is a very definite hindrance to concentration on the work in hand. Also, the conferees are apt to tie up the laboratory telephone while issuing orders concerning their new plans. These activities of officials and foremen are not being derided. They are recognized as quite essential but, patently, they could be effectively handled elsewhere. How and where that is to be done is management's affair. If the laboratory is well-directed and unhampered it will make personal calls by foremen in quest of tests unnecessary by promptly reporting results of all tests.

The needs of all departments should be studied and correlated. Laboratory records should be consulted to determine the nature and volume of work required by each and the responsible heads should be called on for suggestions. Samples should be classified according to a general rule of precedence which may be set aside or modified when occasion warrants. A schedule of testing and reporting should be arranged for those departments which submit a large number of samples. Ordinarily there is a congestion of samples the first thing in the morning and a choice must be made of those to be handled first. Unless some rule is applied the selection will be haphazard and important samples may be delayed. If conditions were constant the choice would be the same each day. Actually, changes in operation and fluctuation in shipping demands shift the focus of attention from department to department. These variations can be met with a minimum of lost time only with the cooperation of all departments. The laboratory should be given notice of changes affecting the sequence of important samples in time to issue instructions for re-routing. By thus giving the most urgently needed samples the right of way each day the departments concerned are assured of tests at the earliest possible moment. It follows, of course, that these tests must be immediately reported and the proper OK's issued to permit preparation of the shipment.

TRANSMITTING THE REPORT

In this connection a telautograph is of value. Through its use the reports on samples can be sent to the departments at the earliest possible moment without the necessity of locating an individual on the phone. Instead of the usual garbled phone conversation, the foreman gets a written record, copy of which is on file at the laboratory.

Where the telautograph or teletype is not available full use should be made of the inter-department telephone. If the other party is apt to be out intermittently a schedule for reporting should be adopted. This should not be too difficult in routine work where each department's samples can be routed and scheduled for completion at substantially the same hour each day. In cases where these tests cannot be immediately reported by reason of the absence of the foreman, a later hour should be selected when he is sure to be in. It is much better to make the laboratory responsible for reporting rather than expect the foreman to call up for his tests. The truth of this statement can be seen from the fact that the urgency will vary from day to day as also will the pressure under which the foreman may operate. Some busy day he will forget to call the laboratory for tests until just before he needs the oil. Then he finds his sample off-test or, Heaven forbid! untested. Such a situation has been known to turn the air blue, curl the hair, or even lose a man his job.

A well-integrated system of supervision and reporting plus departmental cooperation can prevent these calamities. The laboratory supervisor ordinarily can determine from past records the approximate hour each day when the tests for each department will be complete. If he then establishes a routine for reporting to each department at a certain hour or hours the process becomes automatic. To illustrate: consider a crude distillation unit which provides several samples for distillation and several for full physical tests. An elementary time study may show that the majority of these samples is completed at nine o'clock. Then at nine o'clock the laboratory supervisor should collect all the available tests for this department and report them. After a few days nine o'clock will be a definite reminder to report to the crude distillation unit. The distillation foreman will note the regularity and grow to depend upon it. Adaptation of this plan to other departments will cut down the constant ringing of the phone and the frequent complaints of poor service. This is not a hard and fast plan but it will take care of the routine samples which come in day after day. For those special samples coming in at odd hours and requiring immediate action, the only answer is full-time, competent supervision.

The causes of friction between technical and manufacturing staffs outlined here have been selected as typical of average conditions. They do not apply directly to every plant but they do reveal a condition to be met in the majority of refineries.

Determination of Lead in

Leaded Motor Fuel

W. N. EPLER
Kanotex Refining Company

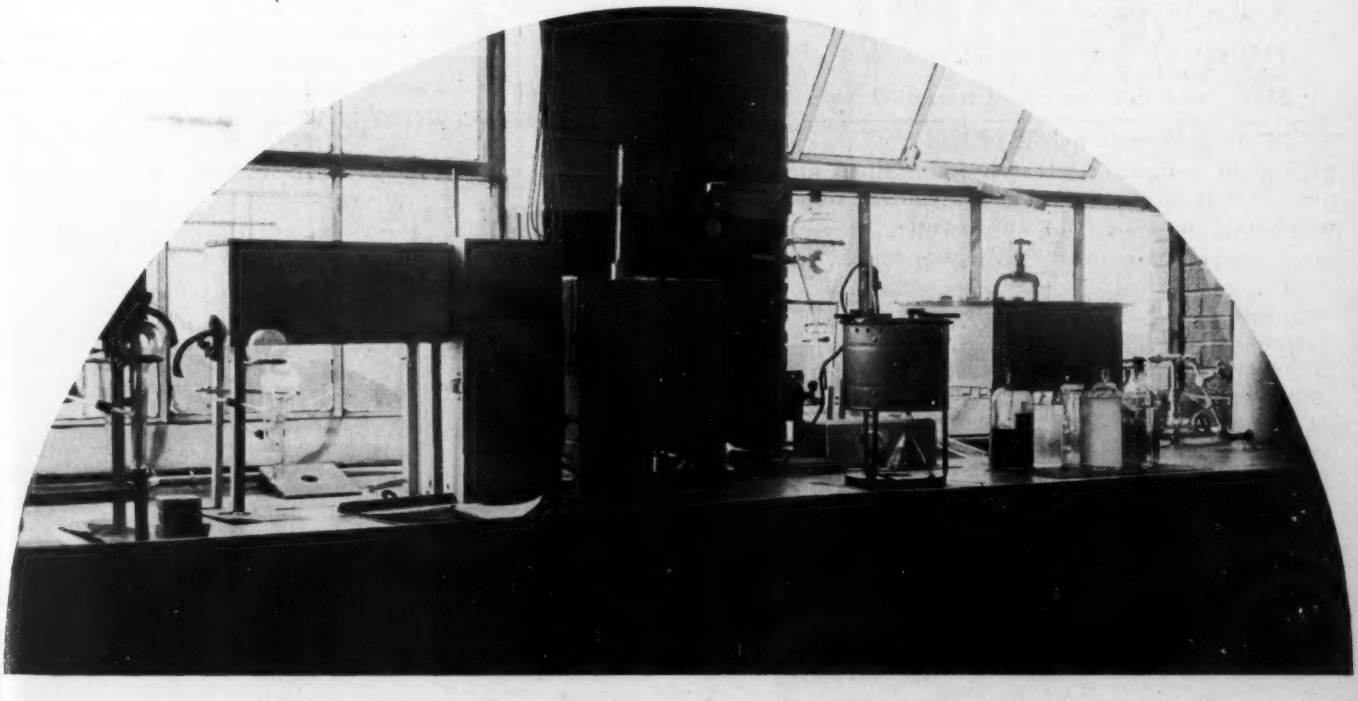
IT IS often desirable to know the amount of lead that a sample of motor fuel contains. A combination of standard procedure gives accurate and dependable results.

First obtain a true representative sample of the product to be analyzed, and measure by some accurate means 100 cubic centimeters to be used as the sample, and place it in a 600 cc. beaker. Add to this sample 100 cc. of straight-run kerosine. (This is to dilute the sample so that it will not be so hard to add the bromine.) Cool the sample and diluent in an ice bath which is under a hood. Add bromine solution very slowly with constant stirring for there is a great amount of heat given off when the bromine is added. The person who is performing the analysis should wear rubber gloves that extend to the elbow while the bromine is being added. A solution of sodium bicarbonate is used to neutralize the bromine if any is spilled on the skin or clothing, as it makes a very bad burn and will discolor the clothing. The bromine should be added until a permanent brown color is obtained, the change in color can be misleading for the bromine reacts with the dye in the sample to produce quite a color change but as more is added the desired brown color will appear and then fade out as the right amount is approached. The lead bromide is usually a light pink.

Filter with suction through a Gooch crucible that has an asbestos mat and which has been dried in an oven at 212° F. for at least 30 minutes. It is not necessary to weigh the crucible. Return this crucible to the original beaker and put a few cc. of concentrated nitric acid in it, then add 100 cc. of 10 percent nitric acid to the beaker and boil until the lead bromide is dissolved. With a stirring rod, loosen the mat in the crucible and wash it with distilled water and remove it from the beaker.

The next operation is to boil the nitric solution to dryness which must be done with care or the thick solution, at the last, will pop out and spoil the determination. The dryness can be obtained by using a hot plate or an electric heater. As the solution approaches the state of dryness, lift the beaker by a pair of tongs, tilting it so that the solution which remains is collected at one side of the bottom. Keep the beaker in a rotating motion so that the bottom is kept moist although the solution only remains on it a short time. In this manner the entire solution may be evaporated to dryness without the loss of any of the sample.

When dryness has been reached remove from the heat and allow to cool so that it may be held in the hand before adding distilled water to dissolve the



lead nitrate. If this is not done, there is danger of cracking the beaker by the addition of cold water.

Add about 75 cc. of distilled water and stir for a few minutes and filter to remove the asbestos mat from the crucible, washing the asbestos on the filter with another 25 cc. of distilled water.

Add dilute ammonia hydroxide solution until the solution turns litmus paper blue. Add dilute acetic acid solution until the solution turns litmus paper red.

While the solution is cold add 15 cc. of N/10 normal ($K_2 Cr_2 O_7$) potassium dichromate, which should give a yellow precipitate. Heat this solution until the precipitate collects in large crystals and readily settles to the bottom of the beaker.

Filter the solution through a Whatman No. 44 paper or equivalent. Wash the precipitate twice with 15 cc. of distilled water at each washing. Collect the filtrate in a 500 cc. Erlenmeyer flask and cool to 60° F. Add 10 cc. of potassium iodide solution and enough concentrated hydrochloric acid solution to liberate the iodine which turns the solution a light brown. Titrate with N/10 normal ($Na_2 S_2 O_3$) sodium thiosulphate solution until the brown color begins to fade and add 2 cc. of starch solution which turns the solution dark blue, then titrate to the end point which is the changing of the blue solution to a clear colorness one.

This is a measurement of the amount of ($K_2 Cr_2 O_7$) potassium dichromate which was not required to precipitate the lead as ($Pb Cr O_4$) lead chromate. This titration must be subtracted from the amount of N/10 normal $K_2 Cr_2 O_7$ being added which was 15 cc., giving the amount of $K_2 Cr_2 O_7$ used by the lead that was contained in the sample.

Multiply this amount by the factor .248 which gives directly the number of cc. of tetraethyl lead that was contained in the sample.

To those who wish to know the origin of the factor .248 some explanation is necessary. The titration is first evaluated as lead equivalent by the formula

$$\frac{(A-B) \times .006907 \times 1000}{\text{Sample}} = \text{Grams per liter total lead}$$

A—B = Amount of $K_2 Cr_2 O_7$ which reacted with the lead in the sample.

This value is changed to the equivalent of tetraethyl lead by the factor

$$\frac{323.4}{207.0} = \frac{\text{molecular weight of tetraethyl lead}}{\text{molecular weight of lead}}$$

giving the weight of tetraethyl contained in the sample. This is converted to cubic centimeters of tetraethyl lead per gallon by the factor

$$\frac{37.85}{1.65}$$

Then by combining these into one factor we obtain the expression

$$\frac{.6907 \times 323.4 \times 37.85}{207.0 \times 1.65} = .248$$

The lead which we wish to determine appears in the form of tetraethyl lead which is dissolved in the fuel. This is reacted upon by bromine which produces lead bromide that is insoluble in the fuel.

$$Et_4 Pb + Br_2 \rightarrow Pb Br_2$$

This is the pink precipitate which is filtered from the motor fuel. This is treated with nitric acid

$$PbBr_2 + 2HNO\ Pb(NO_3)$$

changing the lead to the nitrate which is very soluble in water. The solution is then made basic with ammonium hydroxide

$$Pb(NO_3) + NH_4 OH \rightarrow Pb(OH)_2$$

changing the lead to the hydroxide. This solution is acidified with acetic acid changing the lead

$$Pb(OH)_2 + 2HAc \rightarrow Pb(Ac)_2$$

to the acetate which is the desired form for precipitation. The $K_2 Cr_2 O_7$ is added in excess which forms the

$$Pb(Ac)_2 + K Cr O_3 \rightarrow Pb Cr O_4$$

lead chromate that precipitates from the solution leaving the excess $K_2 Cr_2 O_7$. This is measured by allowing it to free iodine from KI solution.

$$4HcL\ K_2 Cr O_4\ KI\ KIO \rightarrow 4KcL\ Cr O_3 + I_2 + 2H_2 O$$

Which is determined by titration with $Na_2 S_2 O_3$

$$2Na_2 S_2 O_3 + I_2 \rightarrow Na_2 S_4 O_6 + 2NaI$$

using starch as an indicator. The starch reacts with the free iodine in a very complexed equation which gives the dark blue solution as long as free iodine remains in the solution.

In preparing the solutions that are used in this determination some explanation is necessary.

The bromine is diluted with an equal volume of carbon tetrachloride for convenience in using and to lessen the danger while being handled.

To make a N/10 normal solution of $K_2 Cr_2 O_7$, 4.904 grams are used in 1000 cc. of water.

To make a N/10 normal solution of $Na_2 S_2 O_3$, 15.8 grams are used in 1000 cc. of water.

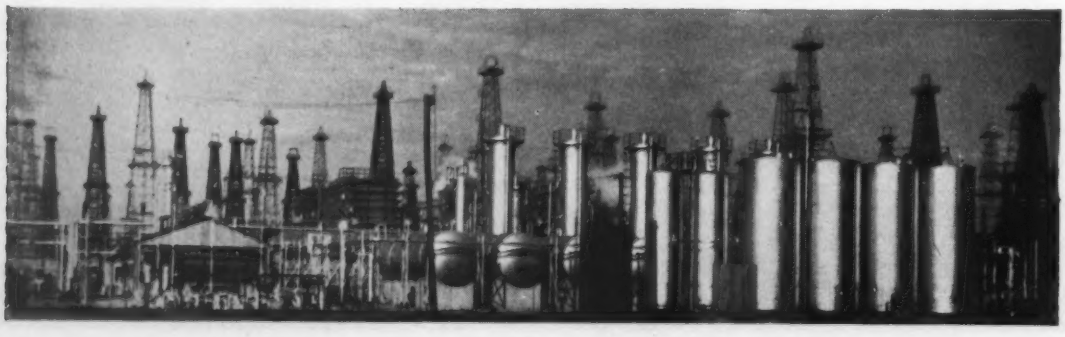
The iodine solution contains 500 grams of ($NaC_2 H_3 O_2$) sodium acetate, 48 grams of (KI) Potassium iodide, dissolved in and made up to 1000 cc. with 25 percent acetic acid solution.

Starch solution which is used as an indicator is made from soluble starch added to water and heated.

With this method and procedure, the desired results may be obtained in less time than with the method that is commonly used.

ACKNOWLEDGMENT

Thanks are due to Mr. F. A. Deering, refinery superintendent, and Mr. Harold Bottomley, research chemist, The Kanotex Refining Company for their co-operation in preparing this discussion.



Three columns used by Carter Oil Company in Grisso gasoline plant to produce any grade of natural gasoline or special products.

Operation of Special Columns *In* Gasoline Plant

WITH three columns installed and operating in the special fractionating department of the Grisso Gasoline Plant, in the north side of Greater Seminole, Oklahoma, Carter Oil Company produces practically any grade of natural gasoline, in addition to turning out commercial grades of propane, butane and pentane. The raw gasoline is manufactured principally in the Grisso plant, located in the same yard, but a considerable amount of it is produced by other plants in the field, as well as heavier condensate from drips and booster station discharge accumulators. The natural gasoline made in distant plants is transferred by pipe line, with the heavier condensate made in the booster stations arriving in the plant through other lines. Drips are picked up by truck when cooler weather prevails, all of which are mixed with the regular production in as near equal proportions as possible, so that the composition of the feed to the fractionators will remain fairly constant.

The average gasoline after being blended in the supply tanks in the plant runs about 93° A.P.I., and contains about 3 percent ethane, 12 percent propane, 24 percent iso and normal butane with the remainder being pentanes and heavier. The composition of this gasoline is somewhat irregular, due to the drips, compression gasoline, with low gravity, and general operating conditions. Considerable attention is given the receipt of regular natural, as well as drips and compression gasoline so that the feed to the fractionators will not vary too widely. The production from other plants is received regularly, which does not offer a problem, but drips and compression gasoline are received intermittently, and are placed in separate tanks so that these products may be fed to the stabilizer or fractionating columns in a regular manner. The battery of tanks from which the gasoline is pumped to the fractionators is arranged so that blending may be easily accomplished and a fairly constant composition may be maintained. But with all precautions, weather and other conditions which affect the operation of a natural gasoline plant will cause an abrupt change in the composition of the production.

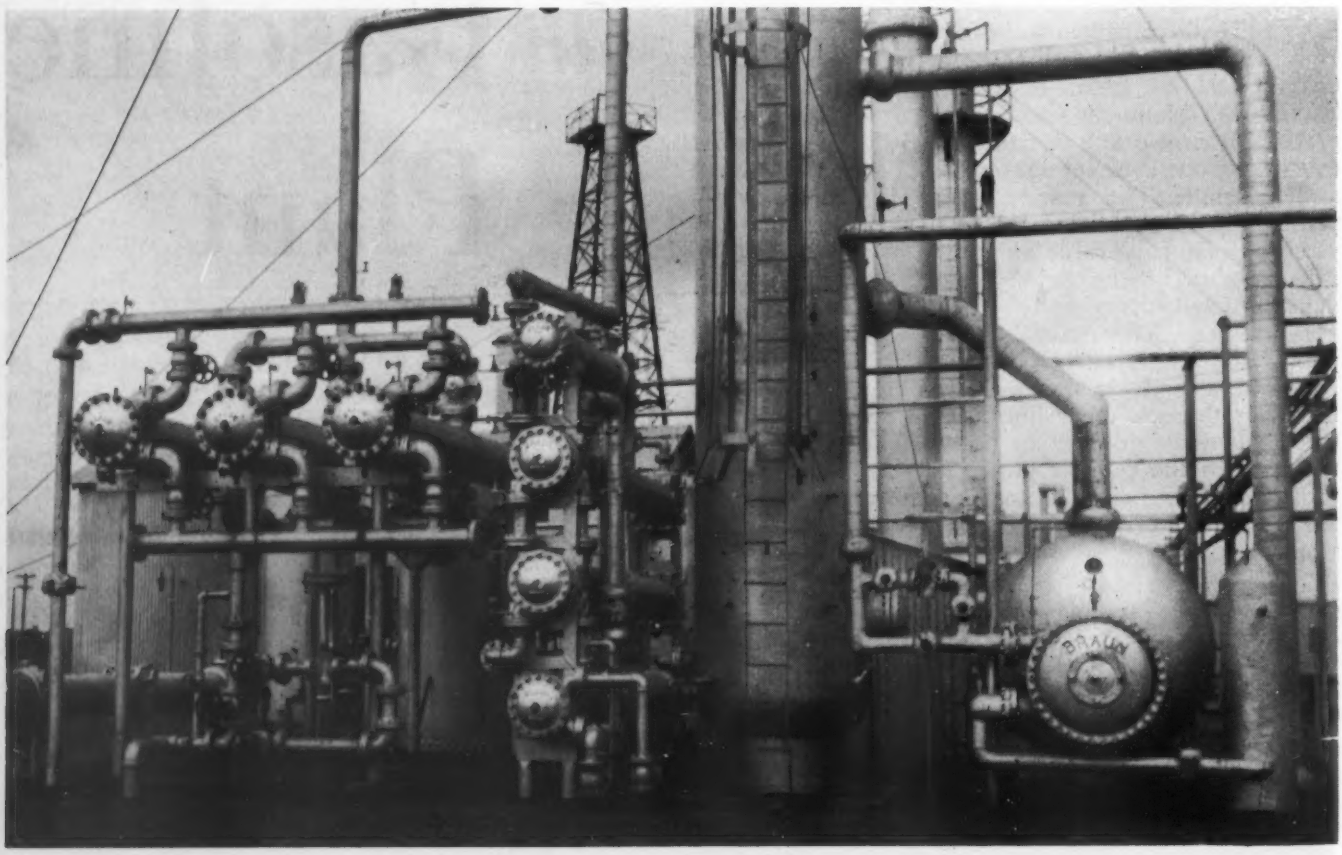
The fractionating system contains three columns, each equipped with its complement of charge-to-production exchangers, base heaters or reboilers, reflux

pumps and accumulators and adequate control instruments. The first column, through which the raw gasoline passes, is 48 inches in diameter and 73 feet in height, containing 33 bubble trays and 7 nozzles through which the feed enters the column. The gasoline removed from any of the storage tanks after being blended to obtain a uniform composition, is pumped to this column under a discharge pressure of 250 pounds, gauge. The temperature of the raw, unstabilized gasoline may vary with the season, but ordinarily it will average about 75° F. Three shell-and-tube bottoms-to-charge exchangers are used to bring the temperature of the raw feed up to about 200° F. to enter the column on the sixteenth tray, or the middle injection nozzle. The point selected for the charge to enter the column may be through any one, or a combination of several, injection nozzles, but that one which has a temperature more nearly approaching that of the feed is used in the majority of instances. The feed line leading to the column is connected to the manifold with seven openings, each being equipped with gate valves in the usual manner for control.

The base temperature of this column is ordinarily maintained with steam at a temperature of about 280° F. so that two products may be obtained from the column. The top of the column controlled with liquid reflux, pumped back over the tower, enables the operator to pass practically butane free vapors overhead, and propane free gasoline from the base. When operating on this type of gasoline, the overhead temperature remains constant at 135° F. Several variations of operation may be maintained, but, when low vapor pressure natural gasoline is desired, together with a propane free butane, and a butane free propane, the pressures and temperatures are generally followed as outlined above.

Gasoline without any appreciable trace of propane leaves the base of the column under processing pressure, to travel counter-current through the 3 feed-to-bottoms exchangers and through a water-cooled after-cooler to reduce temperature. Vapors from the top of the column, fractionated from the charge, and containing a small amount of ethane, are permitted to pass against a reflux ratio of about 25:1. The reflux ratio is calculated upon the amount of overhead production, instead of the amount of feed to the column. Twenty-five times the amount of overhead vapors is recirculated, after being condensed in shell and tube condensers, cooled with water. This reflux ratio is maintained only when it is desired to produce a butane free overhead, so that the base product will carry all the butanes and heavier hydrocarbons. When other methods of operation are being carried out, as for example, the production of straight 26/70 natural, temperatures and reflux ratios are changed so that only the essential butanes are left in the column with the production to obtain this quality of natural.

In the majority of gasoline plants, where special fractionators are operated, as well as simple gasoline stabilizers, the temperature in the base of the column, or the reboiler, is controlled from a point nearby, which allows the introduction of steam for temperature maintenance. This column, instead of being controlled at a point within the base of the column or at the reboiler outlet, is controlled from a thermometer well placed upon the thirteenth plate.



Stabilizer in Carter Oil Company's Grisso gasoline plant, greater Seminole, used in conjunction with two other columns when making special products from natural gasoline.

It has been observed that when an even temperature is held at about this point in the column more efficient fractionation can be obtained due to the fact that a considerable part of the necessary separation has already taken place in the lower part of the column. The temperature recorder-controller employed to obtain a reboiler temperature of about 280° F. is adjusted to operate with a considerable lag in controlling the input of steam to the tubes of the heating element, because of the length of time required for a given volume of vapors to reach the controlling point in the column. The action of the control valve on the steam inlet is quite slow, opening gradually as the temperature at the thirteenth plate is lowered due to any change in the composition of the feed, and closing as slowly when the temperature rises above the degree of heat required. As the process followed in operating the first fractionator is for the purpose of eliminating practically all of the propane and lighter fractions from the column charge, controlling the reboiler temperature from a point well up in the column has been found to be quite efficient.

The initial pressure obtained by pumping the raw gasoline to the first fractionator of this series, is sufficient to carry liquids and vapors on through the system without the need of additional pumps or compressors. The vapors leaving the top of the first column consist of practically pure propane, with only the small amount of ethane. Only the amount of vapors are condensed that are required to maintain the desired reflux ratio of gases removed to liquefied gases returned, with the excess passing on through the accumulator drums as vapors. Condensation and cooling of the reflux are obtained by controlling the volume of water flowing through the shell and tube condensers with a liquid level instrument on the side of the reflux accumulator. Sufficient level is maintained in this vessel to carry on column control so that condensation of overhead vapors need not be exactly constant.

The function of the second column is that of controlled weathering to remove ethane and moisture from the propane. The pressure carried on this column is around 235 pounds, gauge, with a base temperature of 110° F. Overhead vapors, carrying practically no propane are vented to a gathering system through which they, together with other undesirable products of fractionation, pass through a transportation system to other points in the field. The propane, liquefied and purified of all lighter hydrocarbons, is trapped out of the base of the column through a line leading to a calcium oxide drier, erected a short distance from the column. This apparatus was made by using heavy casing, constructed with bolted manhole covers in the top so that lime may be added when needed, and with flanged hand hole openings near the base so that spent materials may be removed. With all water vapors removed from the liquefied petroleum gas, the propane travels, still under processing pressure, to pressure storage.

Bottoms from the first fractionator, butane and heavier, pass to the third column for further treatment. The third column is operated with a pressure of 120 pounds, gauge (when making an eleven pound natural) with the reboiler temperature carried at about 280° F. This column is one of the older type units of bottle-neck construction, with the lower half larger than the upper. It was originally designed with reflux condensers attached to the vapor outlet, but others have been substituted and placed on supports near the ground, for convenience. With close cut fractionation, this battery of columns operates more efficiently when a certain predetermined volume of liquids is returned to the top by pumping.

When on stream for fractionating a sufficient amount of the butanes from the charge to the third column, an overhead temperature of about 170° F. is obtained by returning a sufficient amount of liquefied butane vapors to the top of the column. The reflux ratio when on this type of operation is 6:1, overhead vapors condensed, to that produced by fractionation. Gasoline is removed through adequate charge-to-bottoms exchangers and after-coolers so that the temperature will be sufficiently low for chemical treating when making a doctor sweet, non-corrosive gasoline.

By combining the operation of the three fractionators, any grade of natural gasoline or special cuts may be obtained by varying the pressure and temperature, the reflux ratio and rate of throughput. Batch charges have been made quite frequently to these columns when producing a commercially pure pentane cut from the gasoline after it has been debutanized. The usual grade of natural produced from the fractionators runs from an eleven pound product to a fourteen pound product.

This plant, and others in the field, are operated so that as much of the propane as possible can be extracted from the gas, by extra cooling of the absorption oil, or by combining a cold oil and an increased gas-oil ratio in the absorbers. With a cooler oil, much of the lighter fractions can be recovered without overloading the distillation equipment. Butane recovered from the regular "make" is used in small quantities at various plants as a refrigerant to obtain unusually low temperatures on the absorption oil. Large quantities are handled by distributors locally, and in various parts of the state for gas manufacture.

The average amount of raw gasoline processed daily through the 3 fractionating columns is about 40,000 gallons. When processed for making 11-pound Reid gasoline, the percentages are, 25,000 gallons of 11-pound natural, 11,000 gallons of butane and 3000 gallons of propane. The ethane absorbed from the field gases, equalling approximately 3 percent of the raw gasoline makes up the remainder of the gallonage.

Additional Research Into

Petroleum Emulsions

Should Prove Profitable

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PETROLEUM emulsions are either a blessing or a curse to the oil man. A large number of emulsions are made in which petroleum forms a major portion thereof, and such emulsions are beneficial in numerous ways; but especially so to the oil marketer in that sales outlets thus are provided for a wide variety of petroleum fractions for which there would otherwise be but slight demand. On the other side of the picture is depicted the ever-present problem every producer of crude oil has to meet; and that is the recovery of pipe line oil from oil field emulsions. With the hope that it will be of value to these producers, an outline of this problem together with suggestions for its solution will be given first. A brief summary of the types of beneficial emulsions of petroleum will then be given.

OIL-FIELD EMULSIONS

Petroleum oil in underground strata frequently is in close contact with water in such strata. Such water generally contains varying amounts of salts in solution and frequently also contains water-insoluble particles in suspension. Further than this, in the Mid-Continent, Gulf Coast and California oil fields the crude itself contains asphalt and asphaltic tars.

The theory generally accepted that tends to explain the formation of emulsions may be stated briefly. When extremely fine particles of one substance are dispersed in a liquid the resulting mixture is called a colloid. Colloids may be divided into two broad groups. Such colloids as have an affinity for water and which may be dispersed completely therein are called emulsoids or hydrophiles. Examples of hydrophilic colloids are: glue, starch, sodium or ammonium soaps, etc. Colloids that are not dispersed readily in water but which are easily dispersed in liquids other than water are called hydrophobes. Examples of hydrophobic colloids are: egg yolk, asphalt, coal tars, gas carbon, insoluble calcium salts, etc. Emulsions are mechanical mixtures of two or more liquids that are ordinarily immiscible and such emulsions can be formed only in the presence of a suitable colloid. The most common types of emulsions are formed from oil and water. If a hydrophilic colloid is present in the water, an emulsion formed from such water with oil is normally of the oil-in-water type in which the droplets of oil are coated individually with extremely thin films of water. Examples of this type of emulsion are: pigmented paints and varnishes, butter, margarine, fresh milk, medicinal salves, etc. However, if a hydrophobic colloid is present in either the oil or the water, an emulsion therefrom formed is generally of the water-in-oil type in which tiny droplets of water are coated with very thin films of oil. Practically all oil field emulsions are of the water-in-oil type.

BREAKING EMULSIONS

Keeping in mind the fundamental facts that emulsions are formed only in the presence of colloids; that water-in-oil emulsions are formed most readily in the presence of hydrophobic colloids and oil-in-water emulsions in the presence of hydrophilic colloids; and that the film of oil enclosing the minute droplets of water in water-in-oil emulsions is very tenacious; the problem of breaking water-in-oil emulsions resolves itself into the removal or decomposition of the hydrophobic colloids therein or the rupturing of the oil films surrounding the water droplets and thereby permitting the coalescing of such droplets into drops which may settle by gravity from the oil.

In cases where the hydrophobic colloid present in the oil field emulsion is asphalt, such asphalt may be removed by means of chemicals which have a strong preferential solvent action on asphaltic compounds. Parenthetically, it has been found that any of those compounds that are used successfully for the solvent refining of lubricating oil also serve to break water-in-oil emulsions in which asphalt is the emulsifying agent. However, as a rule the cost of using solvent-refining chemicals for breaking oil field emulsions is prohibitive in that relatively large proportions of such chemicals dissolve in the treated oil or in the water and sludge separated therefrom. Chemicals which actually react with asphaltic compounds in emulsions are not used because of the fact that such chemicals either react with the treated oil also or else with the water present to form compounds that are detrimental to the quality of the oil or that corrode the pipe lines or tanks containing the treated oil.

Due to the fact that in nearly every instance an oil field emulsion contains not only asphalt but other hydrophobic colloids as well, the problem of breaking such emulsions must be attacked from an angle other than that of removing the asphalt from the crude oil. The attack therefore settles on the rupturing of the oil film encasing the individual water droplets. Oil films may be broken in numerous ways. The emulsion may be heated sufficiently to cause the water droplets to expand and thereby reduce the surface tension of the oil to such an extent that the oil films will break and thus permit the water to coalesce and settle. This is the oldest known method of breaking oil field emulsions. The emulsion may be agitated with copius quantities of pure water. This method operates successfully only on those types of emulsions in which the hydrophobic colloid present is partially soluble in pure water; thus

permitting the washing out of the colloid itself from the emulsion.

In cases where the water present in the oil field emulsion contains electrolytes in solution, it is possible to break such an emulsion readily by passing an electric current through the emulsion. This serves the double purpose of heating the emulsion and thereby reducing the surface tension of the oil films and of changing or neutralizing the electric charge on the film and thus reducing its power to adhere to the water droplet. Electrical dehydrators are used quite extensively for breaking oil field emulsions, especially in localities where electric power rates are low. The most obvious advantage of electrical treatment over chemical treatment of emulsions is that there is no possible contamination of the treated oil with harmful chemicals or residues.

If a hydrophilic colloid is introduced into an emulsion which already contains a hydrophobic colloid, the two colloids tend to oppose each other and thus the surface tension of the oil films become nil and the water droplets coalesce rapidly. In other words the added colloid tends to form an oil-in-water emulsion from the water-in-oil emulsion and thus reduces the adhesive power of the oil films therein to such an extent that the water droplets break through these films and settle by gravity from the oil, thereby breaking the emulsion completely. In order to be truly effective in breaking the emulsion the hydrophilic colloid should be readily dispersible in the emulsion itself and its rate of solution in either the oil or water should be comparatively slow. Due to the fact that glue, starch, and colloids of a like nature are not readily dispersible in an oil field emulsion, such compounds may not be used successfully for this purpose. However, sodium and ammonium soaps are true hydrophilic colloids; are readily dispersible in oil field emulsions; and their rates of solution in the oil are extremely slow. Therefore such colloids comprise the bulk of the compounds used for breaking such emulsions.

USE OF SOAPS

Soaps are essentially inorganic esters and may be in the solid, liquid or paste form. Only the liquid soaps are used for breaking oil field emulsions. Such soaps are normally formed by the hydrolysis and esterfication of vegetable or animal fats by means of caustic or ammonia. It has been found that if certain vegetable fats, particularly castor oil, are first sulfated with concentrated sulfuric acid and then either partially or wholly saponified with caustic or ammonia, the resulting compound is a liquid that is readily dispersible in a water-in-oil emulsion and has a very slow rate of solution in petroleum oil. Therefore such sulfo-soaps, as they are called, form the base product from which nearly all oil treating chemicals are made. To this base may be added other liquids which, in the main, tend to reduce the viscosity of the soap or render it more readily dispersible in the oil field emulsion.

In brief, the method of making a sulfo-soap from castor oil comprises mixing concentrated sulfuric acid with pure castor oil under rigid control of temperature; allowing the acid to remain in contact with the oil for a predetermined period; washing the excess acid from the sulfated oil with water or a sodium sulfate solution; and then saponifying the washed oil with an ammonia solution or a solution of caustic and ammonia. It will be noted that there are so many variable factors present that an almost unlimited number of sulfo-compounds or bases may be formed in this manner. Upon the concentration of the sulfuric acid used and the amount thereof depend the degree of sulfation of the castor oil. The temperature at which sulfation occurs and the time of contact of the sulfuric acid with the castor oil are variables which must be kept under rigid control in order that the reaction product may be duplicated. The amount of water used in washing the sulfated castor oil (which is insoluble in water) is a variable in that any free sulfuric acid remaining in the mixture after washing will react with the caustic or ammonia which is added later and so cause undesirable side-reactions to occur during saponification. Also the strength of the caustic or ammonia solution and the proportion thereof used are variables which determine the degree of saponification of the sulfated castor oil. The degree of saponification will likewise determine the proportion of glycerine present in the finished base. Glycerine is a by-product of saponification and is regarded generally as beneficial in emulsion-breaking compounds. When it is considered that castor oil is but one of the many vegetable or animal fats that may be sulfated and then saponified, it may be realized that the services of an experienced oil-fat chemist are required to make sulfo-soaps for use in breaking emulsions.

"Sludge acid," or the acid remaining from the acid treating of petroleum fractions is sometimes used as such ore is neutralized with ammonia and then is used as a compound for breaking oil field emulsions. Also naphthenes may be sulfated and then neutralized with caustic to produce a base frequently used in the compounding of emulsion-breaking chemicals.

OTHER PETROLEUM EMULSIONS

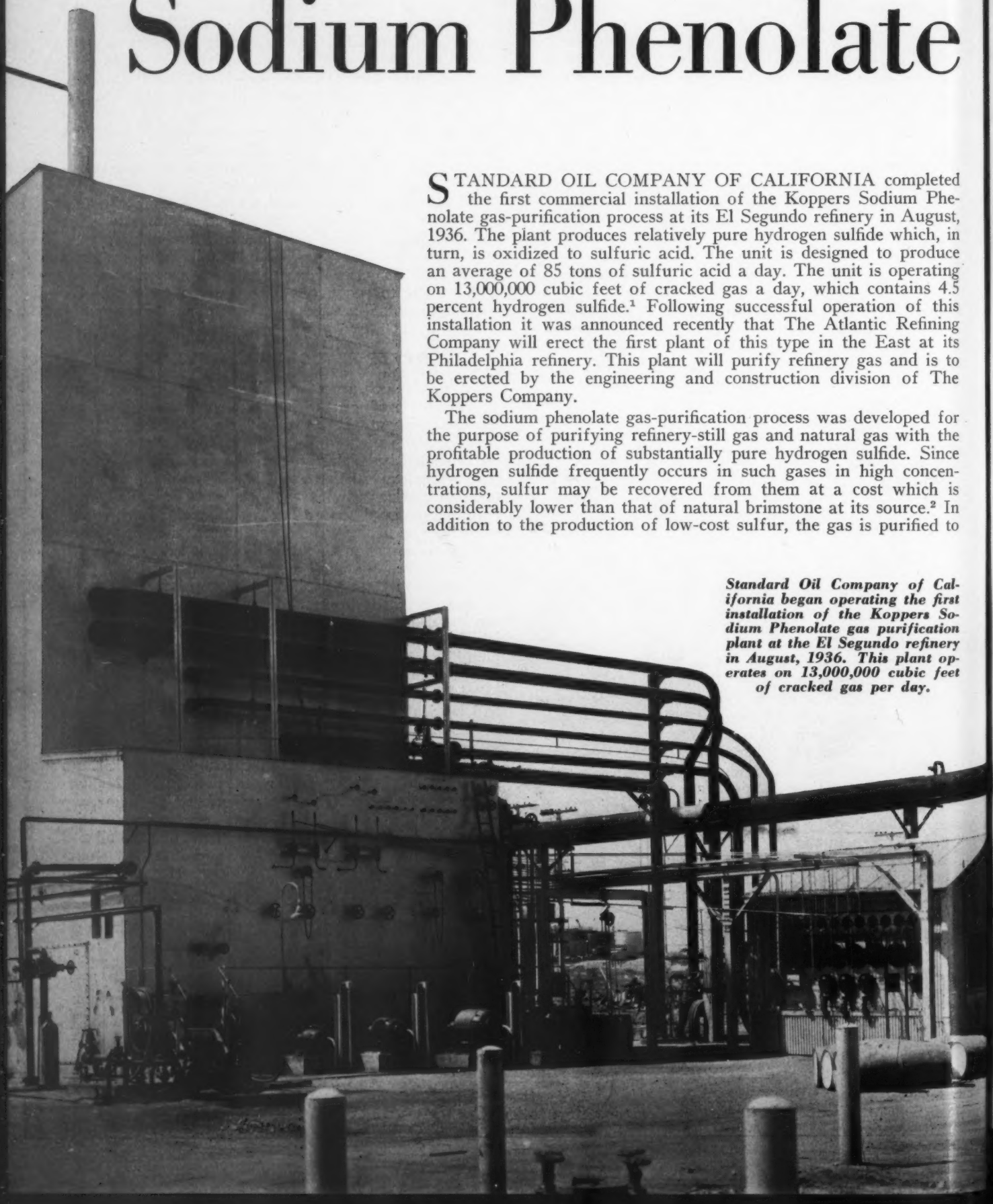
There are such a great number of types of emulsions formed or produced with petroleum or its fractions as a component that it would require several pages just for the listing of them. Therefore only a few of the so-called beneficial types will be noted here. Petroleum asphalt may be emulsified with water in numerous ways to produce emulsions that are used as paint, road building material, or roofing compounds. Such emulsions may be of the water-in-oil type or the oil-in-water type; depending on the colloid that is added. Various types of steam-engine lubricants and practically all greases made from petroleum are emulsions. Nearly all of the so-called dormant sprays used in horticulture are emulsions of petroleum fractions with water to which insect poisons are sometimes added. Sodium plumbite solutions used for doctor treating gasoline are in reality emulsions of oil, water and an insoluble colloid. Carbon black may be emulsified with glycerine and lubricating oil to form printing inks. Emulsions of sodium soaps with petroleum oil and small amounts of water are used to remove "hardness" from water by forming insoluble calcium soaps with the calcium compounds in such water. The oil present in the emulsion forms a protective film around the calcium soap as soon as it is formed; thus permitting such impurities to be filtered from the water. Emulsions of road oil and water are much more satisfactory for dust-laying purposes than either water or oil alone. Heavy fuel oil emulsified with a zinc chloride solution is used for preserving wood. Sewage may be clarified by emulsifying it with petroleum oil. Emulsions of heavy petroleum oil and water may be heated in the presence of a small proportion of air to form a fixed combustible gas which has a high calorific value. Most important of all from the standpoint of future research is the interesting proposal to render gasoline conducting by emulsifying it with an electrolytic solution and then pass an electric current through this emulsion to precipitate the gums

[*Continued on page 93*]

Gas Purification *with* Sodium Phenolate

STANDARD OIL COMPANY OF CALIFORNIA completed the first commercial installation of the Koppers Sodium Phenolate gas-purification process at its El Segundo refinery in August, 1936. The plant produces relatively pure hydrogen sulfide which, in turn, is oxidized to sulfuric acid. The unit is designed to produce an average of 85 tons of sulfuric acid a day. The unit is operating on 13,000,000 cubic feet of cracked gas a day, which contains 4.5 percent hydrogen sulfide.[1] Following successful operation of this installation it was announced recently that The Atlantic Refining Company will erect the first plant of this type in the East at its Philadelphia refinery. This plant will purify refinery gas and is to be erected by the engineering and construction division of The Koppers Company.

The sodium phenolate gas-purification process was developed for the purpose of purifying refinery-still gas and natural gas with the profitable production of substantially pure hydrogen sulfide. Since hydrogen sulfide frequently occurs in such gases in high concentrations, sulfur may be recovered from them at a cost which is considerably lower than that of natural brimstone at its source.[2] In addition to the production of low-cost sulfur, the gas is purified to



Standard Oil Company of California began operating the first installation of the Koppers Sodium Phenolate gas purification plant at the El Segundo refinery in August, 1936. This plant operates on 13,000,000 cubic feet of cracked gas per day.

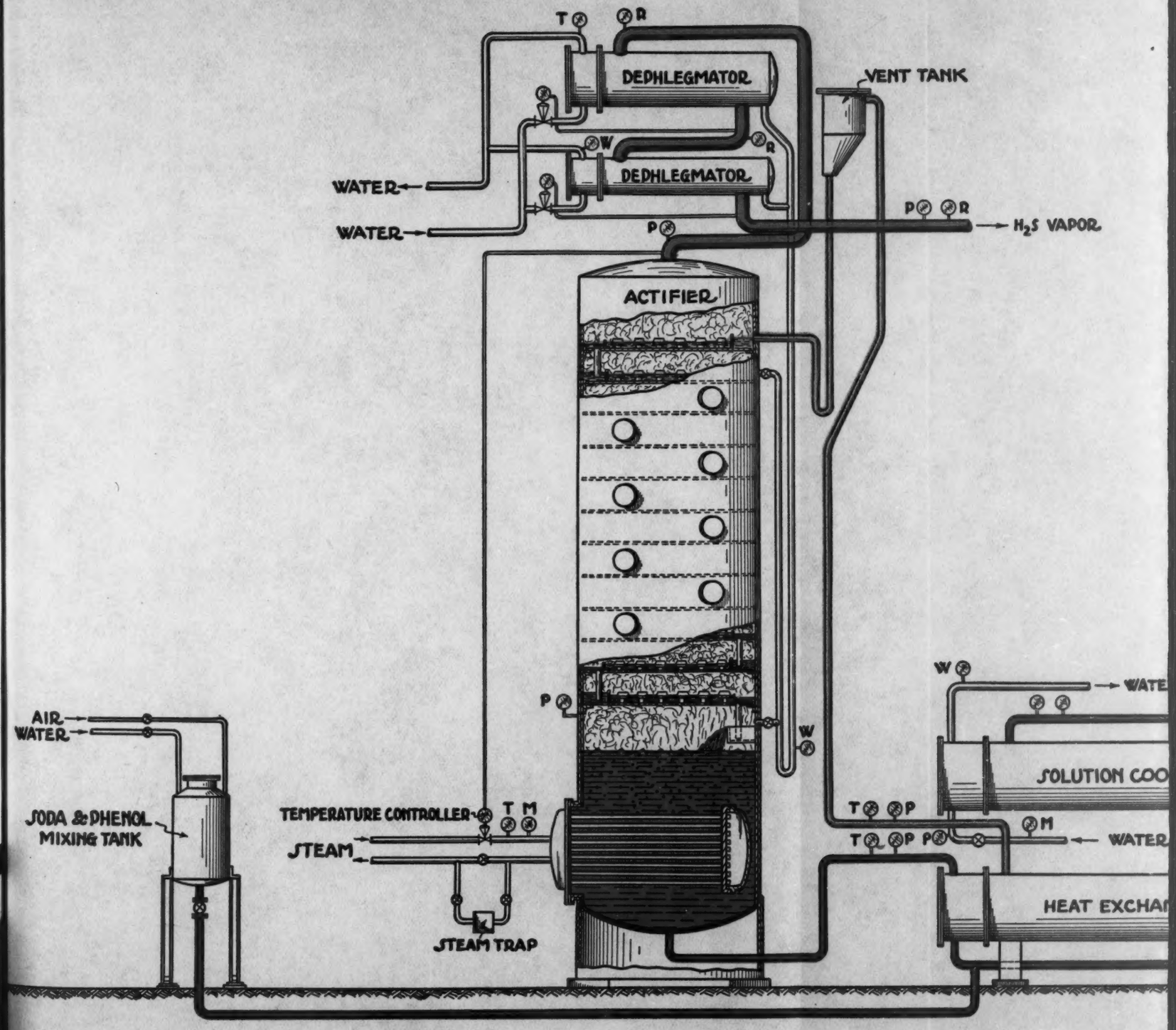


FIGURE 1

Koppers liquid purification system for natural and refinery still gases—Phenolate p

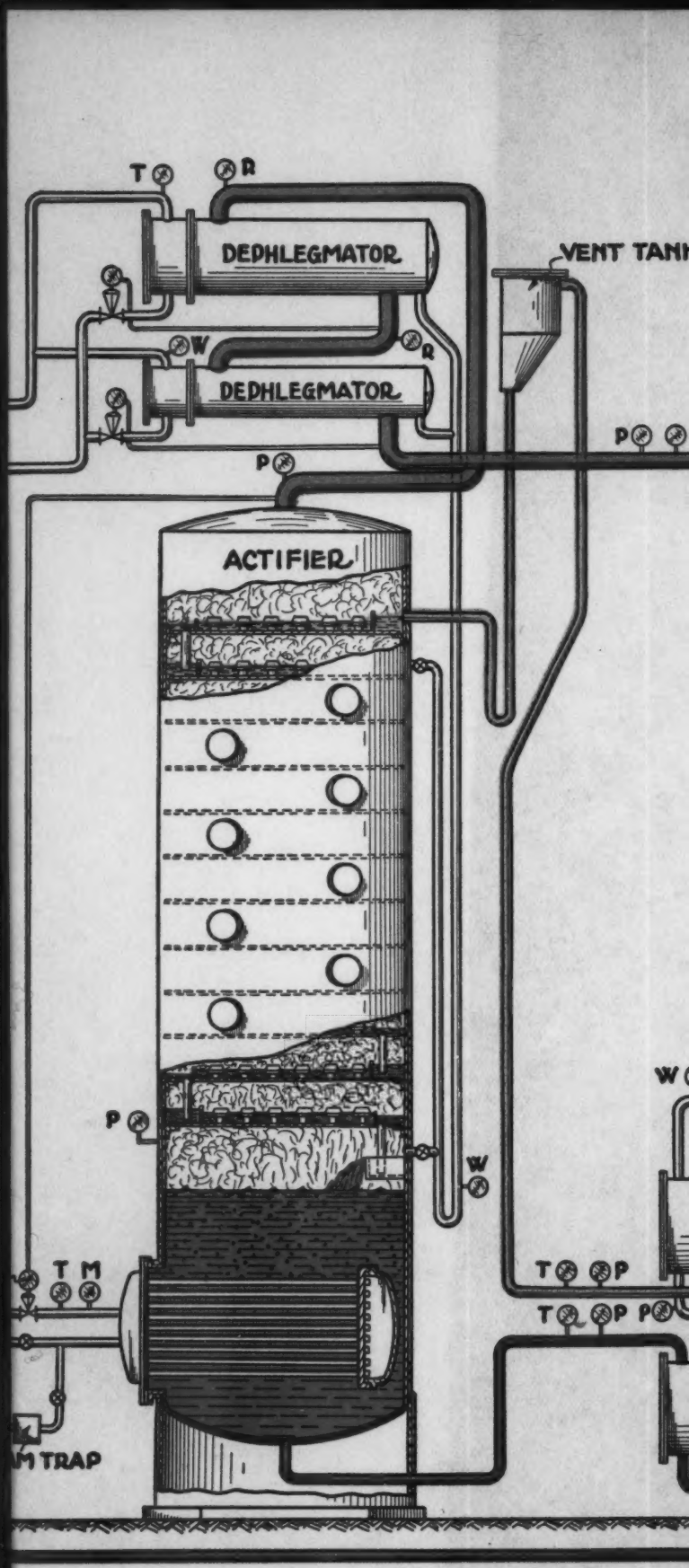
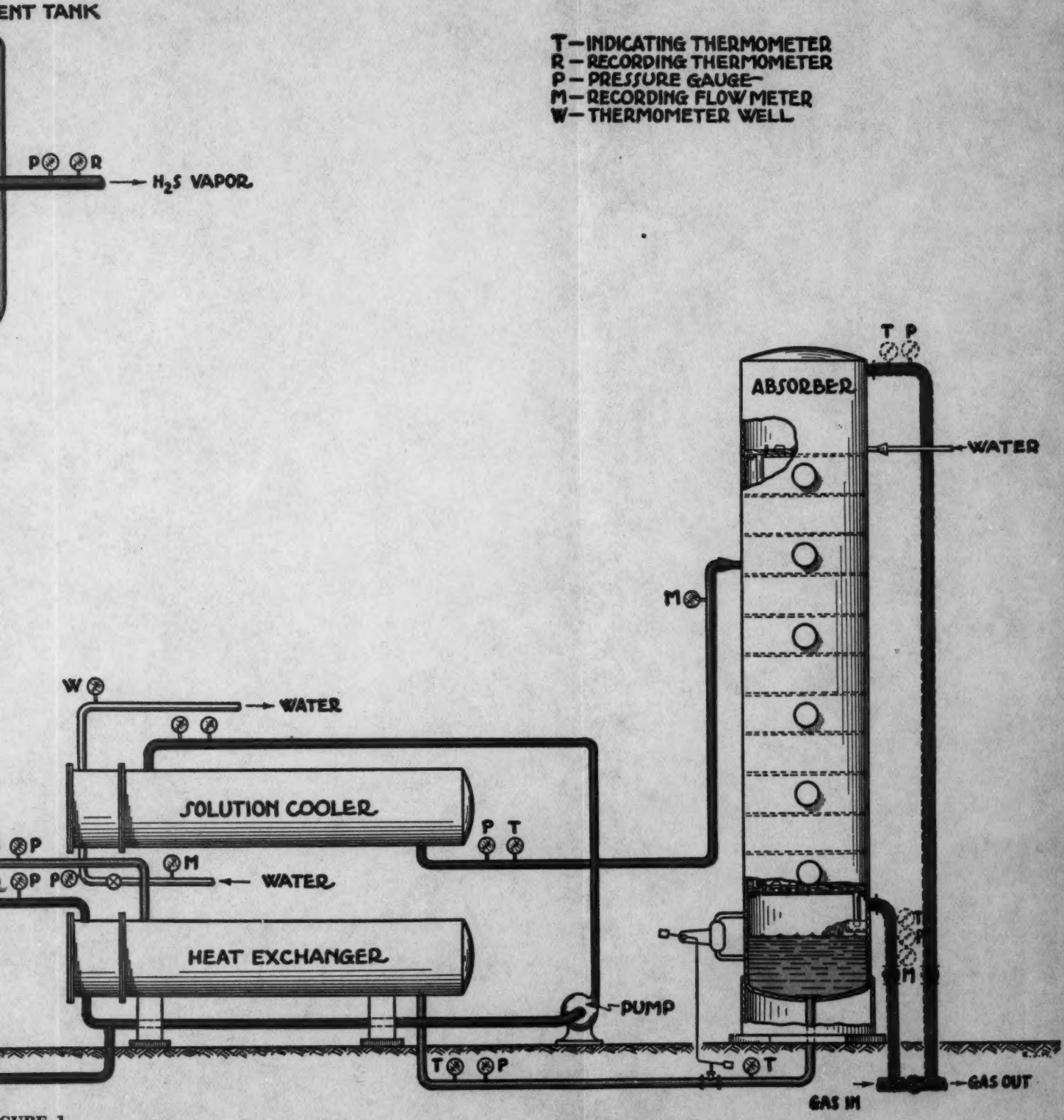


FIGURE 1

Koppers liquid purification system for natural and re



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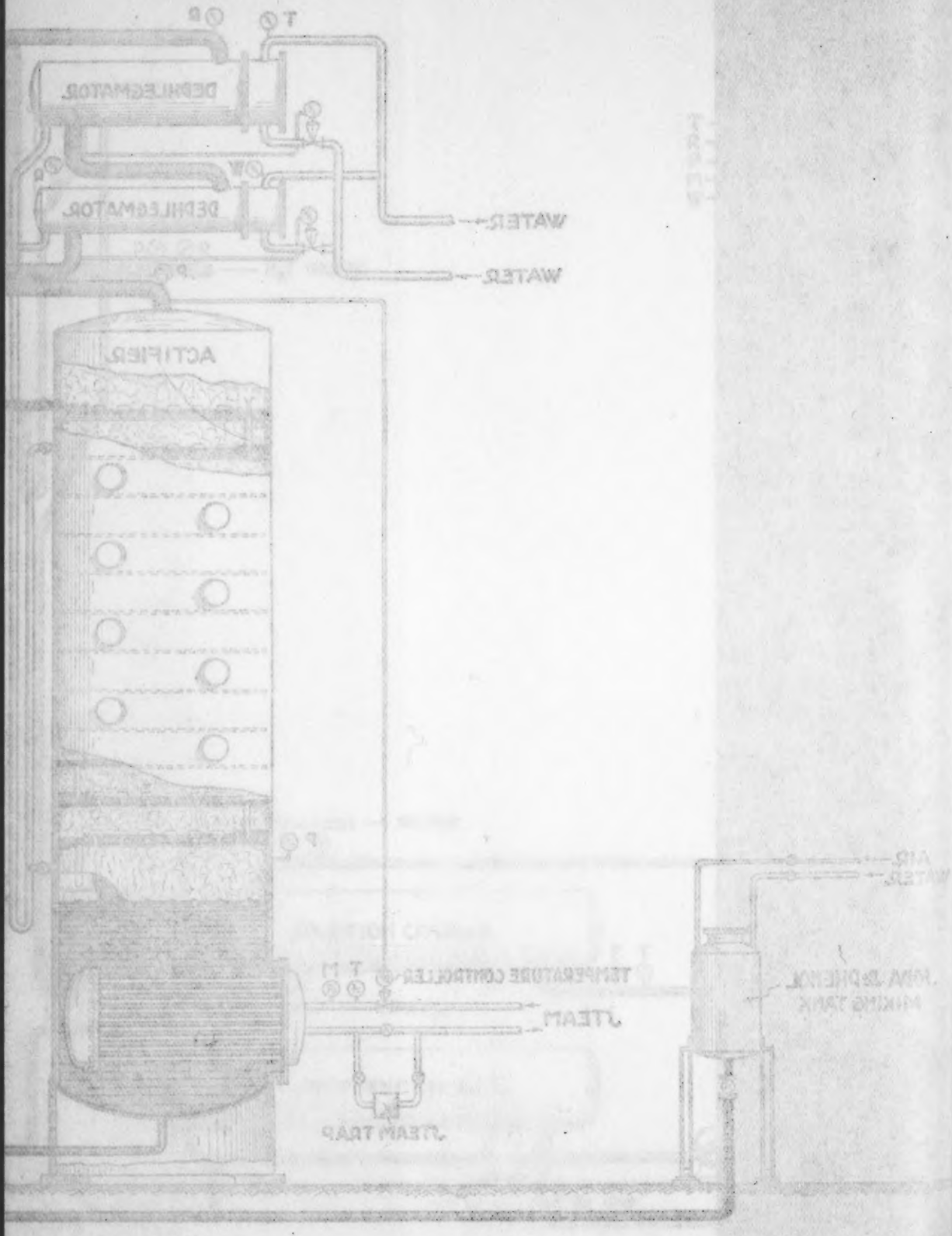
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STEAM TRAP

the extent of 95 percent to 99.8 percent. By this type of process the refinery gas is prepared for further treatment in a polymerization unit for production of liquid products.

Sulfur recovered by the sodium phenolate process is in a form readily adaptable to the manufacture of sulfuric acid by any of the conventional methods. Often there is sufficient sulfur in the cracking-still gas generally burned under boilers to supply the acid requirements of the entire refinery, and at a cost which may be as low as 50 percent of contact acid cost. Acid plants of modern type used for converting hydrogen sulfide gas into sulfuric acid are simple compact units which are practically automatic in their operation and require no special type of labor and supervision other than the usual refinery personnel.

SIMPLE APPARATUS

The purification system consists of an absorption stage and an actification stage through which the sodium phenolate solution is continuously circulated. This solution has a high carrying capacity for hydrogen sulfide, amounting to 2000 to 4000 net grains per gallon. As a result, it is necessary to circulate only five to ten gallons of solution per thousand cubic feet of gas. The low circulation rate contributes to low operating expense and the simplicity of equipment required.

Referring to the flow diagram, Figure 1, the hydrogen sulfide-laden gas enters the absorber at the base, passes up through the bubble-cap trays and leaves at the top, stripped of 95 percent of its hydrogen sulfide. The solution leaving the bottom of the absorber, saturated with hydrogen sulfide with respect to the incoming gas, passes through the heat-exchanger tubes, to the top tray of the actifier. It flows down over the actifier trays, counter-currently to the stripping steam which is generated in a reboiler at the base. Sufficient indirect steam is used to effect the desired degree of actification of the solution. This, in turn, is determined by the maximum residual hydrogen sulfide desired in the exit gas.

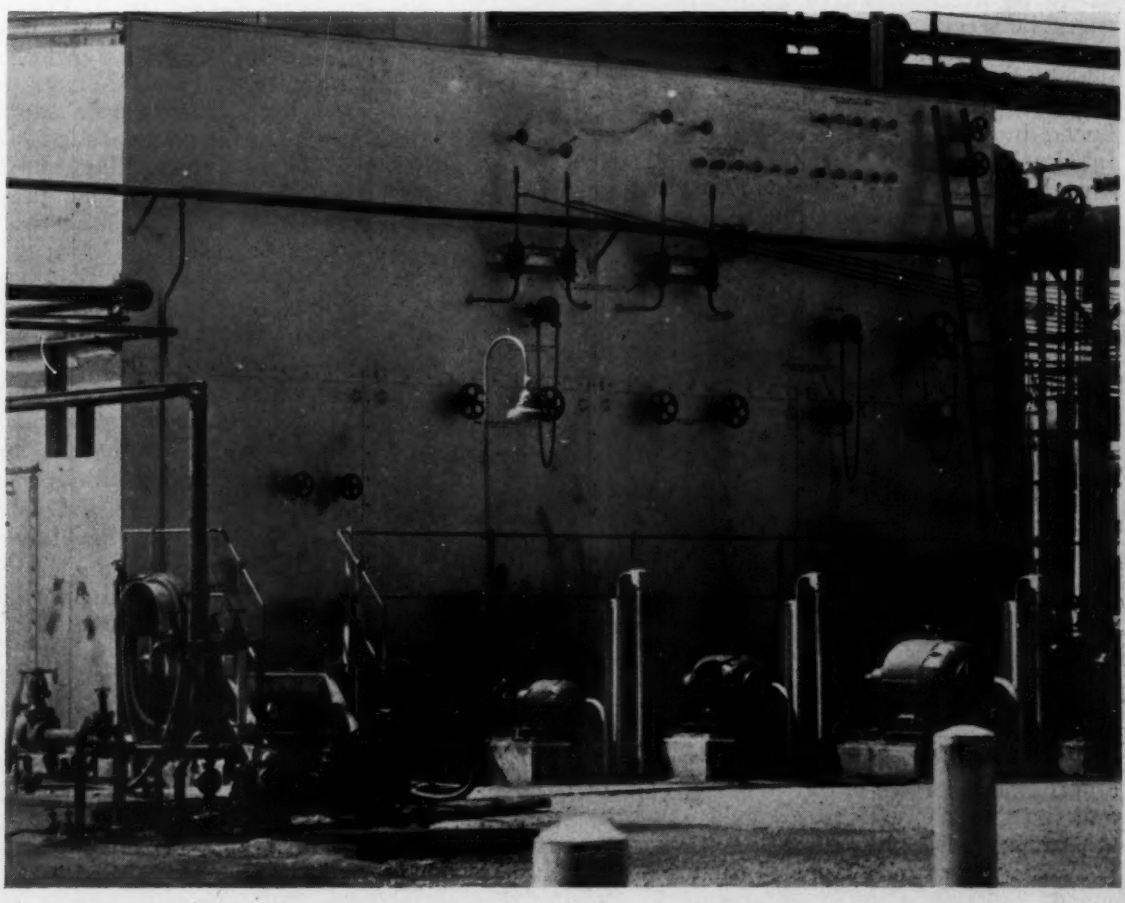
The actified solution flows from the reboiler through the heat-exchanger shell, is further cooled in the solution cooler, and is then pumped to the fourth tray below the top of the absorber. The absorption cycle starts again at this point.

Hydrogen sulfide-laden steam passes from the top of the actifier to the dephlegmator shell and from here the hydrogen sulfide is forced, by means of the actifier pressure, to the acid plant burner or other point of disposal. Condensate from the dephlegmator returns to the actifying column.

Fresh water is added continuously to the top tray of the absorber. The three top trays comprise, in effect, a water scrubber to recover chemicals which have been entrained or evaporated from the solution. It is necessary, at intervals of several days, to replenish chemicals lost from the system and a small mixing tank is provided for this purpose. The caustic soda and the crude phenol used in the process are relatively inexpensive.

The plant to be erected for The Atlantic Refining Company at Philadelphia will be able to recover the hydrogen sulfide from 22,000,000 cubic feet per day of refinery still gases at 225 pounds pressure. The hydrogen sulfide may be converted to sulfuric acid and the purified gas will be further processed by polymerization.

[1]Egloff, "Cracking and its Economic Significance," Refiner, Vol. 15, No. 12, December, 1936, page 544.
[2]Refiner, Vol. 15, No. 10, October, 1936, page 476.



Motor-driven pumps circulate the solution in the Koppers gas purification system.

Synthetic Lubricating Oils

By Transformation of Chlorinated Hydrocarbons

(Translated from Petroleum)

THERMAL decomposition of chlorinated hydrocarbons leads to the formation of either resins, tars, drying oils or lubricants, depending on the nature of the raw stock and the treating conditions. In these transformations the chlorine is liberated as hydrochloric acid and the result is usually ring-formation and polymerization of the resulting unsaturated radicals or remaining nuclei.

Most of the researches in this field deal with the use of chlorinated paraffin wax. Suitable paraffin wax is obtained, besides from petroleum, from low-temperature carbonization of coal tar, lignite tars or directly from the waxy products of the Fischer-Tropsch synthesis.

The chlorination is carried out by passing chlorine gas at the optimum temperature through the melted wax with very active stirring and efficient contact between gas and liquid. Iodine acts as a catalyst for this reaction. The presence of iron, copper and aluminum metal acts as a catalyst for the decomposition of the chloro-compound. The material can easily be decomposed or dechlorinated at temperatures between 250 and 350° C., or at much lower temperatures in the presence of aluminum chloride, which is an excellent catalyst for this purpose. Starting with the "Kogasin," boiling over 220° C., produced by the Fischer-Tropsch water-gas synthesis, lubricating oils are produced by chlorination followed by condensation at 130° C., using activated aluminum metal. After the reaction has proceeded for one or two hours at this temperature active evolution of hydrochloric acid gas is evident and the reaction from then on completes itself in about 7 to 15 hours depending on the chlorine content of the raw stock employed. The viscosity of the product compares favorably with that of high grade natural lubricants. Employing higher decomposition or dechlorination temperatures, or a subsequent heating to very high temperatures, will however, exert a bad effect on the general quality of the finished product.

Polymerization is known to be the formation of high molecular weight substances from low molecular weight compounds, of similar type of molecules. By condensation one understands a reaction in which are built up new and usually higher molecular weight hydrocarbons or compounds from low molecular weight compounds of dissimilar substances or hydrocarbons, which latter are quite different in properties from those of the end product. Considerable research has already been completed by those employing aluminum chloride, boron fluoride, etc., as catalysts and the use of cracked unrefined gasoline, kerosene, etc., as sources of olefin materials, as well as the by-products from benzole purification plants which has resulted in producing lubricants of high quality by condensation methods. The reaction can be carried out in liquid or vapor-phase processing.

The condensation of ethylene and naphthalene has been thoroughly investigated at the University of Birmingham. It was shown that at least 20 percent of aluminum chloride as catalyst was necessary, at a temperature of at least 250° C., for complete and rapid conversion. At this temperature the conversion is rapid and at an optimum. The yield of lubricant fractions from the reaction-product is fairly large, but there is always an attendant resinous sludge layer formed at the same time, which is about 30 percent of the original stock. The lubricants thus formed show high densities and high refractive indices. Their stability is less than that shown by the natural lubricants (oxidation stability), even though there is usually no sludge formation. The viscosity index, one of the most important properties of an oil or lubricant is in general poor. The color of these oils is good, and resins are absent. Similar to the above condensations is a Friedel-Craft synthesis carried out on a practical scale in the United States, for the manufacture of a synthetic motor oil, called "Paraflow"; this oil is made from chlorinated paraffin wax using either benzole or naphthalene, and with aluminum chloride as a catalyst; an insert petroleum light oil is used as a diluent. This synthetic oil possesses the very unusual property, that when mixed with an oil of high pour-point in small amounts, of substantially lowering the pour-point of the mixture. Used in larger amounts it is generally employed to improve the characteristics of ordinary motor-oils or inferior oils to the level of high quality lubricants.

The Friedel-Craft reaction has been employed to manufacture lubricants from the high boiling fractions of "Kogasin," obtained in the Fischer-Tropsch synthesis. The results obtained in Germany have been previously published. Subsequent reports of researches carried out at the University of Birmingham show that reactions analogous to or similar to those mentioned above can be easily and efficiently carried out by the use of metallic aluminum instead of aluminum chloride. In this method organic addition compounds containing both chlorine and aluminum are formed, which by subsequent breaking up with water (hydrolysis), neutralization, and a finishing distillation yield viscous lubricants. The new catalytic method for condensing chloro-waxes with the aromatics was next thoroughly investigated. It was found that long paraffin chains are valuable constituents of lubricating-oils. One therefore em-

ploys in such synthesis raw materials containing these long chains, namely paraffin wax; this is then chlorinated. A paraffin wax of 124° F. melting point is chlorinated using iodine as a catalyst, until the mass has absorbed 10, 17.5 and 25 percent of chlorine; this chlorine content represents approximately mono, di and trichloro paraffin. At best the chlorination does not take place completely and in simple fashion, so that the product containing 10 percent of chlorine already contains small amounts of the di and tri chloro-paraffins.

These chlorinated paraffins were next condensed with various ring-compounds (aromatics) using aluminum metal as a catalyst. In all cases 10 percent of aromatics were used, and the aluminum added in the presence of an inert high boiling petroleum solvent, such as kerosene, in order to keep the mass liquid and facilitate thorough mixing and to maintain a good control of the temperature during reaction. Using solid aromatics such as naphthalene at moderate temperature (above room temperature), and a diluent is of course necessary. When employing the liquid aromatics, such as benzole or its homologues, the reaction proceeds fairly rapidly at room temperatures; in the latter cases, a solvent such as petroleum naphtha is still advisable. When the mono and di chloro paraffin is condensed with benzole, toluol or naphthalene, there resulted semi-solid to solid hydrocarbons of melting points as high as 85° F. The tri chloro paraffin, instead will yield with the same aromatics, clear viscous oils of light color, resembling the natural lubricants. The density and refractive index of the oils made from tri chloro paraffin depend largely on the nature of the aromatic used. Stability of viscosity to changes in temperature or viscosity index is high in all cases.

By the use of aluminum as a catalyst one will obtain excellent yields: 70 to 80 percent of finished oil based on the original raw stock. If instead one employs aluminum chloride as a catalyst with tri chloro paraffin and naphthalene at ordinary temperatures a very rapid reaction results, accompanied with an exceedingly rapid evolution of hydrochloric acid gas, and the final product is a black rubbery mass.

The use of metallic aluminum as a catalyst yields besides high grade lubricants, about 20 percent of a heavy black resin, containing aluminum chloride compounds and which is active enough to be employed in a subsequent or new condensation.

The color of the final oil is decidedly dependent on how completely the resinous or sludgey components are separated from the supernatant oily layer.

From the residue or sludgey material one can by the use of solvents, extract certain valuable coloring compounds. A small amount of the latter added to very pale oils imparts to them a strong and well-appearing fluorescence.

Emulsions

[*Continued from page 88*]

therein and to render any organic sulfur compounds present reactive to the electrolyte itself; thereby removing such sulfur compounds and breaking the emulsion at the same time.

CONCLUSIONS

In view of the above it is apparent that more research into the problems of making and of breaking emulsions in which petroleum, or its fractions, comprise a part thereof is not only advisable but should be profitable. For example, since the early days in the oil fields, it has been accepted as fact that the only way to determine the effectiveness of an emulsion-breaking chemical was to try out a number of such compounds on large batches of oil field emulsions at the point where such emulsions have been produced. The reason given for this inefficient and costly practice has been that a sample of such an emulsion could not be shipped any distance without at least partially breaking. This seems to be a very poor excuse when it is realized that efficient and inexpensive laboratory-size colloid mills are available and that a sample of a "broken" oil field emulsion may be fully re-emulsified simply by passing it through one of these colloid mills. In fact, samples that have been stored for several months have been completely re-emulsified as needed by the aid of a colloid mill. Therefore much time and money may be saved and more efficient use of chemicals may be had if the field men would send samples of their actual oil field emulsions in to a central laboratory where such samples may be used as needed for testing the effectiveness of the emulsion-treating chemicals being used or proposed. The research laboratories of nearly every large oil company contain one or more such colloid mills and these mills could be used for the above purpose in addition to their use in the preparation of experimental types of emulsion.

REFERENCES

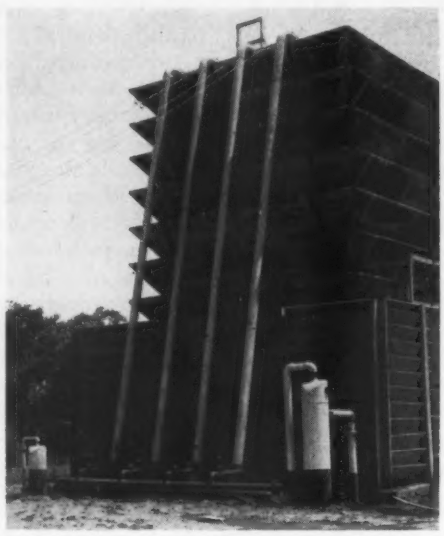
(Author's Note: The author has available copies or briefs of at least 126 technical articles, 37 textbooks, and 196 U. S. and foreign patents all relating to emulsions or the breaking thereof. The scope of this article does not permit inclusion of all these references; hence this bibliography is limited to those books which are considered to be most pertinent to this subject.)

"Industrial Oil Engineering," Battle.
"The Examination of Hydrocarbon Oils, Fats & Waxes," Holde-Mueller.
"Examination of Petroleum Products," Hamor & Padgett (1920).
"A.S.T.M. Tentative Book of Standards," 1925.
"Lubricating Greases," E. N. Klemgard (1927).
"The Chemistry of Leather Manufacture," J. A. Wilson, A.C.S. Monograph (1923).
"Technology of Oil, Fats & Waxes," Lewkowitsch. Vol. I, II & III, (1923).
"Hydrocarbon Oil & Saponifiable Fats & Waxes," Holde (1922).
"Textile Soaps & Oils," Hurst & Simons (1921).
"Outlines of Industrial Chemistry," F. H. Thorp (1921).
"The Carbon Compounds," C. W. Porter (1924).
"Theory of Emulsions & Emulsification," Wm. Clayton (1921).
"U. S. Bureau of Mines Report of Investigations No. 2683," March, 1925, D. B. Dow.
"U. S. Bureau of Mines Report of Investigations No. 2688," March, 1925, D. B. Dow.
"U. S. Bureau of Mines Report of Investigations No. 2692," May, 1925, D. B. Dow & Reistle.
"U. S. Bureau of Mines Bulletin No. 250," D. B. Dow.
"Second Colloid Symposium Monograph," A. J. Starm (1925).
"Fourth Colloid Symposium Monograph," Brian Meads & J. T. McCoy.
"Fifth Colloid Symposium Monograph," (1928).
"Edible Fats & Oils," Eldson (1926).
"A Manual of Dyeing," Knecht, Rawson et al, Vol. II (1925).
"The American Soap Makers Guide," Stanislaus & Meerbott (1928).
"Vegetable Fats & Oils," Geo. S. Jamieson, A.C.S. Monograph No. 58.
"Properties and Uses of Petrohol," 1st Ed. (1932).
"The Castor-Oil Industry," U. S. Dept. Agri. Bulletin No. 867, J. H. Shrader (1920).
"Technical Aspects of Emulsions," Third Ed. by 17 Authors (1936).

IDEAS to help plant efficiency...

Water Circulation Over Cooling Tower

TO relieve pumps of extra duty, and to conserve steam, J. E. Crosbie, Inc., installed a multiple system of gas jetting in the main cooling tower at the Fitts gasoline plant, to circulate water from the cooling-tower basin over the cooling sections. The cooling-tower basin extends three feet past the end of the tower foundation. Four holes were drilled, cased and cemented for wells in which the water flows from the basin itself. Each well is equipped with a string of pipe and fitted with a gas line to jet the water from the well to the top of the tower. The wells have sufficient depth to secure the necessary submergence for jetting water. The gas is scrubbed through small vessels placed on the gas line in front of the jet columns to prevent contamination of water by oil and other foreign matter flowing with the gas from the residue scrubbers. Adequate cooling of tower water has been secured from the first by this type of circulation system, without cost for steam or other motive power to drive extra pumps.



Water Circulation Unit

Rising Stem Gate Valve Guard

AN easily removed rising-stem gate guard can be made by using pieces of two-inch pipe welded so that one part forms a riser and the other located so it can be slipped over the stem of the gate valve. The riser is of sufficient length that it can be placed in the ground without concrete or grout to stiffen, and when it is necessary to remove the guard, it can be slipped backward and upward at the same time without excessive pulling.

At all points where gate valves are placed in vertical lines, these guards are placed, especially on gas lines to absorbers and to and from scrubbers. The apparatus is both simple to construct and inexpensive and affords protection where it is greatly needed. The guards shown are in service at Carter Oil Company's Fitts gasoline plant.

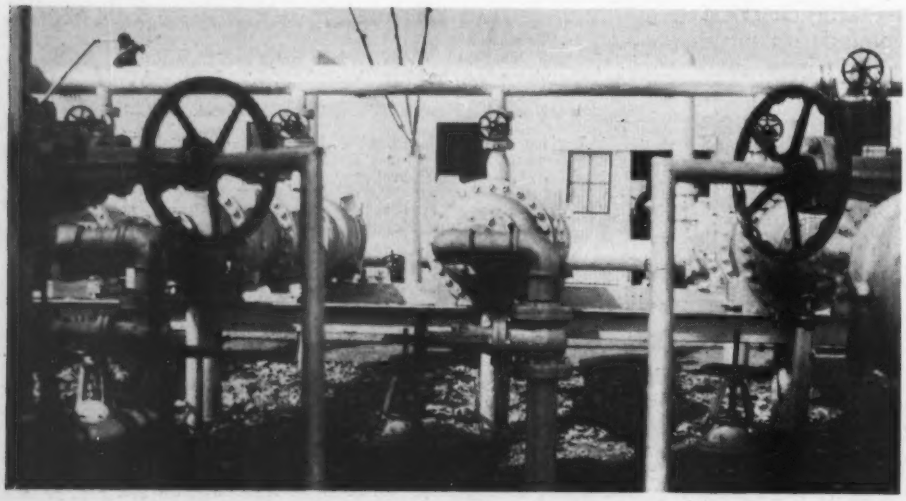
J. C. A.

High Pressure Automatic Scrubber

GAS under a pressure of 1400 pounds is handled in Skelly Oil Company's Cunningham, Kansas, gasoline plant, and the usual after-scrubbers were placed in the stripped gas lines, but to prevent a possible carry-over of liquids which might interfere with gas-lift and repressuring operations in the field, a special scrubber was added. This was placed in the gas line at the point where it left the plant yard.

This scrubber was made in the plant, using good pieces of heavy casing set vertically with the intake line connected to the pipe near the base. The outlet is connected at the top, and a mist extractor in the column prevents liquids from passing out with the gas. A liquid level instrument on the base of the column automatically drains and traps any liquid from the column to the mineral seal oil system in the plant.

Tail, or residue gas scrubber used to remove mineral seal oil after passing from high pressure absorbers en route to field for gas lifting.



Rising stem gate guard

Test for Corrosion

A SIMPLE, quick, yet very sensitive method of running a corrosion test is as follows: Dissolve 20 cubic centimeters of butyl mercaptan in one liter of sulphur-free kerosene for your stock test solution.

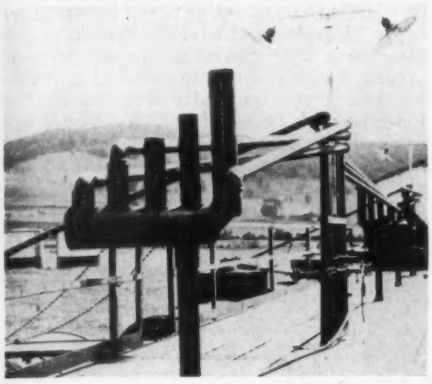
In running the corrosion test, pour approximately twenty five cubic centimeters of the oil to be tested into a four ounce bottle, put five drops of the mercaptan solution into the oil and agitate vigorously. Pour ten cubic centimeters of ordinary doctor solution into the bottle and shake again. Any black or dark brown discoloration or black scum on the surface of the doctor solution indicates a positive corrosion test.

This method is reliable when correlated with the copper strip and is particularly valuable to treaters in plumbite sweetening plants where the oil may go "off corrosion" at any time.

Greggton, Texas. W. S. C.

Loading Rack Swing Funnels

ALLEGHANY REFINERIES, INC., at Bolivar, New York, made loading rack tank car fill pipes all a certain length so they could be used in tank cars not exactly on "spot." The risers enter through the floor of the rack and are fitted with the usual swing joints. Instead of supporting racks built to hold the ends of these loading pipes, a manifold is attached to a line leading to the slop disposal system.



Funnel to prevent dripping gasoline from falling on loading rack walkway.

This manifold was made with five nipples welded at right angles to a larger piece of pipe attached to this riser, so the loading pipes could be inserted in these nipples for drainage. The natural leakage, gasoline and other products, coming from the lines after they had been used fall into these funnels and the small amount saved for rerunning. A clean rack is the result, free from inflammable material which always creates an additional fire hazard.

Temporary Dome Cover

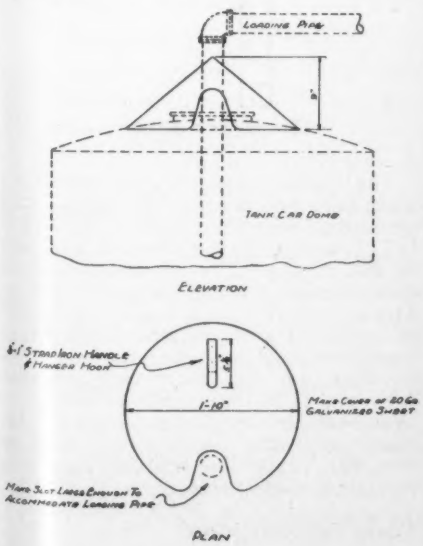
THE sketch shows a temporary tank-car dome cover for use while loading petroleum products during inclement weather.

For gasoline and other light products the cover acts as a diffuser and prevents the evolved vapors from emerging from the car in a continuous column.

For asphalt and fuel, the cover prevents the entrance of rain, snow, etc., in quantities sufficient to cause any difficulty.

The cover is made of No. 20 gauge galvanized sheet and is soldered into form. The drawing is self explanatory.

HAROLD BOTTOMLEY,
Arkansas City, Kansas.



Automatic Drip on Intake Scrubbers

FLUID entering intake scrubbers in gasoline plants and booster stations is removed by several different methods, either automatically or by manual control. In a new station in the Mansion Pool of Oklahoma City, two valves are made to operate in unison. The scrubbers are placed vertically, having skirts upon which the vessel rests, and also having outlet connections in the lower head for the removal of liquids. Outside the vessel, a manifold is provided, one part arranged so that fluids may be removed through a manually operated gate valve, and another for the automatic valve. The outlet from the automatic valve is connected through piping to a buried receptacle which receives the liquid. Lines leave the underground vessel and pass through a second manifold in which a second automatic valve is placed. Operating tubing is connected to a remote control unit located on the manhole cover of the underground vessel, which in turn is actuated by a float arm that rises and lowers as the fluid level changes inside the tank.

The automatic valve on the manifold connected to the scrubber is one which remains open to permit the fluid to drain into the vessel below the ground, but when the fluid level rises to a certain height in that tank, the remote control mechanism begins to function closing the valve at the scrubber and at the same time opening the valve on the outlet connection leading from the underground vessel permitting the fluid to be blown to the proper receptacle in the plant. Reverse operation of the two valves was decided upon so that if for any reason, the outlet valve should become jammed while relieving the buried vessel, the valve on the outlet of the scrubber would remain closed.

Jet Circulates Vapor-Recovery Gasoline

TREATING vapor-recovery gasoline in a refining plant becomes a relatively simple matter when a few gadgets are put to work. Because treating solution brings on constant supervision when it is continuously circulated with pumps, Wilcox Oil & Gas Company made a simple connection on the secondary gasoline storage tank which accomplishes contacting the gasoline with the doctor solution and circulates the chemicals at the same time.

The tank in which the gasoline is placed when it leaves the vapor recovery plant under process pressure is 10 feet in diameter by 40 feet in length. The connection through which the gasoline originally entered the vessel was placed in the lower side of the front head, and when completing the circulating connection, a similar two-inch line was connected to the water drain connection at the back end of the tank and attached to the one entering the tank at the front. To secure adequate mixing and circulation an ejector is fitted in the line where the junction of the circulating line meets the line carrying the gasoline from the accumulator tank to the larger vessel.

Doctor solution is placed in this tank until it reached a depth of about 18 inches, which has been found to be sufficient for adequate circulation and treating. The pressure of the gasoline drained from the plant accumulator under the process pressure is sufficiently high to cause the jetting action neces-high to cause the jetting action.

Treating is semi-batch, in that the gasoline entering the tank is contacted with the doctor solution and remains in the tank until it becomes filled. When sufficient production has been made that the gasoline must be transferred, it is removed through a line attached to the back of the tank hav-

ing a connection or riser inside the shell sufficiently high that no treating solution is removed during the transfer. Pumps are eliminated in this operation, because process pressure upon the accumulator tank is sufficient to transfer the gasoline to the combination treating and storage tank and to cause circulation of the chemicals. Compressed air is used to transfer the gasoline from this tank to storage.

"Loping" Cured in Gas Engine

WHEN one of a battery of vertical gas engines suddenly went temperamental, running as sweetly as its mates for hours on end and then beginning to lope and lose power; all the usual tests of ignition, compression, fuel lines, mixing valve and head gaskets were made, without finding anything wrong—and without accidentally correcting the trouble, as sometimes happens.

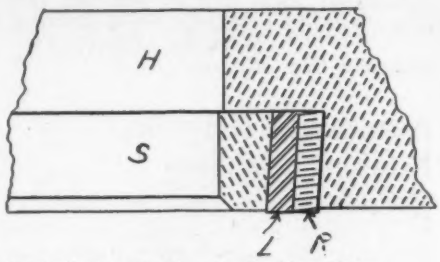
At the first opportunity the engine was shut down, and the head pulled from the cylinder suspected of causing the erratic operation. Immediately the trouble was apparent. The exhaust valve seat—of the inserted type—was held in the cast-iron cylinder head by a ring of soft steel, designed to be peened into the sloping, annular space between valve seat and head.

Under service conditions this locking ring had worked loose, allowing the seat insert to follow the valve down as the cam moved it, the seat sliding in the groove and acting as a sleeve to cut off the exhaust port as effectively as did the valve itself. That particular cylinder was then unable to clear itself of burned gases, and in consequence was prevented from drawing in a full charge of fresh mixture on the suction stroke.

Peening, the method used for expanding the lock ring, "L" in the sketch, failed to hold the seat tightly, and there was no hydraulic press available for upsetting the ring cold and making it serve.

As a last resort, the play being sufficient for the valve seat to be completely removed from the casting, the lock ring was firmly clamped in place, and six equally-spaced holes drilled around the circle on the line between ring and cylinder head. These then were tapped for ¼-inch bolts, the thread being carried full up with bottoming taps.

The lock ring then was pulled, and a thin copper "Dutchman" or shim was cut from 0.004-inch stock so as to fit the bottom of the recess and extend just as far as the locking ring. Over this the seat and



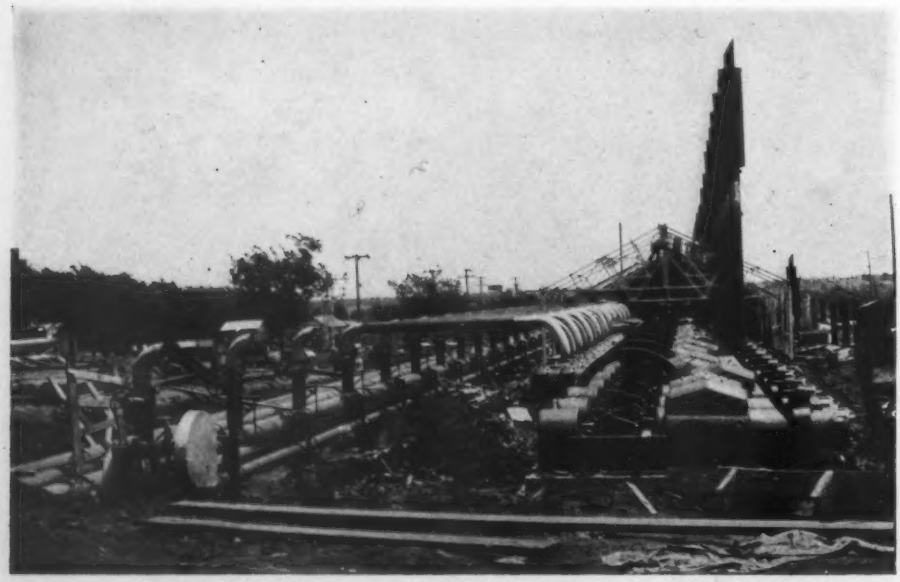
H—Cylinder Head L—Locking Ring
S—Valve Seat R—Retainer Stud
(Not drawn to scale.)

ring were reassembled, clamped tightly in place with the valve, and studs screwed evenly home in the six holes. The excess stud was filed down to the cylinder head, to obviate any possible "hot spot" to cause pre-ignition.

Through the expedient of placing the shim under the lock rim, the halves of the threads in ring and head were thrown out of line by 0.004-inch, bringing the screw pressure against only half the threads in each, and tending to force the ring even tighter into the head. E. S.

Safety Valves on Discharge Header

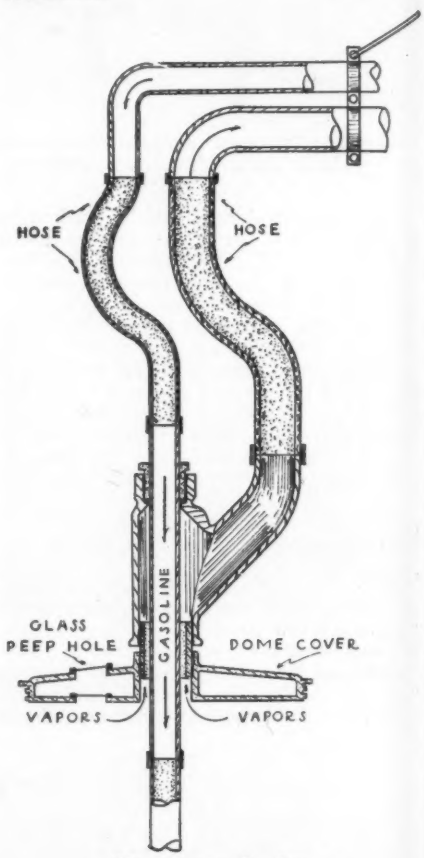
TO be sure that safety valves will operate, should pressures exceed a certain predetermined amount, Phillips Petroleum Company has installed two safety valves on one line in its Mansion Station in Oklahoma City. A relief header laid the entire length of the compressor building terminates at the extreme end in the usual gas-vent stack. At the point where each discharge line from the compressors crosses beneath the vent line, connections are provided to lead excess gas under pressure to the atmosphere. A riser leads from the discharge line and extends well above the walk level, where it is equipped with a tee and other necessary connections for the installation of two safety valves, one on each side of the riser. Each valve will permit gas to flow from the discharge line to the vent line header through separate connections. The valves are not only automatic, but are equipped with a hand lever by which the operator can relieve the pressure instantly and at will.



Arrangement of relief valves on discharge header.

Closed Car Loader

LOADING losses in the refinery are high and in many refineries the rule is to do most of the loading of lighter products at night to eliminate as much evaporation as possible. This evaporation or loading loss can be reduced or eliminated entirely by employing a closed car loader as shown in the diagram. The apparatus should be constructed of as light material as possible so that it can be easily handled by the loading rack men. After the car has been opened the loading dome cover on the loading line is screwed on the dome and the car is ready to be loaded. It is understood, of course, that the cover rotates independent of the rest of the apparatus.



Closed car loader.

The loading cover is equipped with a glass peep hole so that the loading rack men may determine when the car is full. Loading can be done at any time of day in the hottest weather without loss through the use of such a device. The end of the main vapor line should be equipped with coolers using chilled water to condense the vapors due to the fact that the empty cars are filled with air. It is impossible to run a car over with this apparatus in use for the reason that the overflow will back up into the vapor line and be caught in the condensate receiver.

M. E. WOOLDRIDGE,
Ponca City, Oklahoma.